



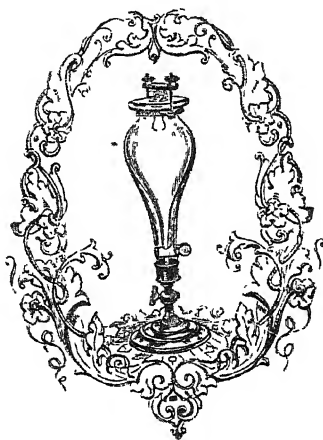
IMPERIAL AGRICULTURAL  
RESEARCH INSTITUTE, NEW DELHI.







WORKS  
OF THE  
CAVENDISH SOCIETY



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OF  
C H E M I S T R Y .

BY  
LEOPOLD GMELIN.

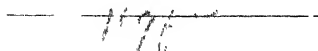
VOL. XV.

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ORGANIC CHEMISTRY.

VOL. IX.

ORGANIC COMPOUNDS CONTAINING TWENTY-FOUR ATOMS OF CARBON



TRANSLATED BY  
HENRY WATTS, B.A., F.C.S.

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(VOL. IX OF ORGANIC CHEMISTRY.)

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# COMPOUNDS CONTAINING 24 AT. CARBON.

*Primary Nucleus*  $C^{24}H^8$ .

## Chrysene.

$C^{24}H^8$ .

C. F. VOGEL. *A. Gehl*, 5, 272.

ROBIQUET & COLIN. *Ann. Chim. Phys.* 4, 326.

LAURENT. *Ann. Chim. Phys.* 66, 136.

PELLETIER & WALTER. *N. Ann. Chim. Phys.* 9, 917; *J. pr. Chem.* 31, 114.

GR. WILLIAMS. *Chem. Gaz.* 1855, 405; *J. pr. Chem.* 67, 248; *Lieb. Kopp's Jahresber.* 1855, 633.

*Vogel's Volatile Amber-resin.*—Discovered by Vogel in 1805. A yellow, mealy powder, which Kidd (*Phil. Trans.* 1821, 212 and 219) observed among the products of the distillation of coal, is perhaps the same compound. (Mansfield, *Chem. Soc. Qu. J.*, i. 248.) The substance observed by Drapiez in crude oil of amber (xiv. 325), and a yellow product obtained by Bussy & Lecanu (*J. Pharm.* 11, 362) in the dry distillation of fat, towards the end of the operation, appear also to consist of impure chrysene.

*Formation and Preparation.* 1. In the dry distillation of amber, when, towards the end of the operation, the acid and all the oil have passed over, and the charred residue is strongly heated, yellow vapours pass over and condense in the neck of the retort. (Robiquet & Colin; Pelletier & Walter.) 2. When the tar obtained in the preparation of illuminating gas from oils and fats is subjected to dry distillation, liquid products pass over at first; afterwards, when  $\frac{4}{5}$  of the tar have distilled over, and the heat is very much increased, a thick oil is obtained, the last portions of which, if collected in a separate receiver, deposit a small quantity of chrysene, while pyrene remains in solution. The remainder of the chrysene condenses in the neck of the retort. (Laurent.)—3. In the distillation of coal-tar, chrysene passes over at a much higher temperature than the dead oil. (Williams.)

*Purification.* Vogel purified the sublimate obtained by method 1 from adhering oil, by dissolving it three times in alcohol, and leaving the solution to cool. Robiquet & Colin boil it for some time with

water, till the oil is volatilized; then melt it, and exhaust the laminogranular solid mass with ether, which leaves the chrysene undissolved. The waxy product is resolved by treatment with ether, and then by repeated boiling with a small quantity of absolute alcohol, into yellow chrysene, which partly remains undissolved, partly crystallises out from the ether and alcohol—and succisterene, which is of paler colour, and ultimately turns white. (Pelletier & Walter.)—The soft, red sublimate in the neck of the retort is detached by scraping and rinsing with a little ether, then triturated and repeatedly boiled with ether, which acquires a red colour by taking up pyrene and the thick oil, whilst chrysene remains in the form of a red powder. (Laurent.)—Williams frees the portion of the sublimate insoluble in ether, from adhering brown oil, by prolonged treatment with ether, and purifies it by re-crystallisation from boiling coal-tar oil.

*Properties.* Shining yellow laminae, resembling uranium-mica. (Robiquet & Colin; Williams.)—Crystalline powder of a fine yellow colour, without any tinge of red or green. (Laurent.)—Soft to the touch; does not adhere to the tongue so strongly as wax. (Vogel.)—Melts between  $80^\circ$  and  $100^\circ$  (Vogel); between  $230^\circ$  and  $235^\circ$  (Laurent); at  $240^\circ$  (Pelletier & Walter); and solidifies to a deep yellow laminar mass on cooling. (Laurent.)—Volatilises completely at high temperatures (Vogel); with partial decomposition, leaving a small quantity of charcoal. (Robiquet & Colin, and others.)—Inodorous and tasteless.

					Laurent. <i>mean.</i>		Pelletier & Walter.		Williams. at 100°.	
24 C	.....	144	....	94.73	.....	93.27	.....	93.10	.....	94.63
8 H	.....	8	....	5.27	.....	5.36	.....	5.84	.....	5.37
$C^{24}H^8$	.....	152	....	100.00	.....	98.63	.....	98.94	.....	100.00

*Decompositions.* 1. Chrysene burns in the air at its boiling point, forming carbonic acid and water (Vogel); on red-hot coals it burns away without emitting any peculiar odour. (Laurent.)—2. With cold oil of vitriol, it turns red-brown with a few violet spots; with hot oil of vitriol, it assumes a fine dark green colour. (Laurent.)—It is only inferior chrysene that is coloured by cold oil of vitriol the pure substance dissolves, with dark greenish blue colour, only in hot oil of vitriol. (Pelletier & Walter.)—3. With bromine, chrysene evolves hydrobromic acid, and forms a brown substance, which decomposes by distillation. (Laurent.)—4. Nitric acid attacks it at a gentle heat, with evolution of red vapours, and, after prolonged boiling, converts it into binitrochrysene, whilst a yellow powder, precipitable by water, remains in solution. (Laurent.)—Vogel and others obtained a resin by treating chrysene with nitric acid.—5. Chrysene dissolves in alcohol containing potash, and separates therefrom as a resin. (Vogel.)—It is not attacked by boiling with ammonia or potash-ley, but colours the latter yellowish. (Robiquet & Colin.)

Chrysene is insoluble in water, also in alcohol. (Robiquet & Colin, and others.)—When impure and contaminated with oil, it dissolves in boiling alcohol. In ether it is but very sparingly soluble; according to Vogel, it requires for solution, 32 pts. of cold and almost as much of boiling ether.—Soluble in chloroform. (Cloeze, N. J. Pharm.

14, 382.); in boiling *oil of turpentine*, rather more freely than in ether (Laurent); easily in *oil of lavender*; scarcely in cold, easily in hot *oil of amber* (Vogel); soluble in boiling *coal-tar naphtha*. (Williams.)

*Nitro-nucleus*  $C^{24}X^2H^6$ .

### Binitrochrysene.

$C^{24}N^2H^6O^8 = C^{24}X^2H^6$ .

LAURENT. *Ann. Chim. Phys.* 66, 140, and 72, 426.

1. Chrysene (p. 1) is boiled for a while with nitric acid, whereupon a red powder separates; the nitric acid is then decanted, and the red powder is boiled with alcohol and dried. The alcohol and the nitric acid retain in solution a yellow body precipitable by water.—2. When chrysene is boiled for a very long time with a large excess of nitric acid, part of it dissolves, and water then separates beautiful orange-coloured flocks, which must be washed and dried.

The product obtained by method 1 is a red powder, like mercuric oxide; the second method yields an orange-coloured powder. (Laurent.)—Pure yellow, and shining; highly electrical. (Williams, *Chem. Gaz.* 1855, 405.)

				Laurent.	
				earlier.	later.
24 C	144	...	59.50	58.29	56.82
2 N	28	...	11.56	11.66	11.80
6 H	6	...	2.48	2.27	2.33
8 O	64	...	26.46	27.78	29.05
$C^{24}X^2H^6$ .....				100.00	100.00

Laurent regarded the products obtained by the two methods as different.

Nitrochrysene, *heated* in a glass tube, melts, swells up, and takes fire with detonation and brown smoke. It detonates on glowing coals.—It dissolves in cold *oil of vitriol*, with brown-yellow colour. Dissolves partially in alcoholic *potash*, and is precipitated therefrom in brown flakes by acids. It is not converted into a base by *sulphide of potassium*. (Williams.)

Insoluble in *water*, scarcely soluble in *alcohol* or *ether*.

*Primary Nucleus*  $C^{24}H^{12}$ ; *Amidogen-nucleus*  $C^{24}Ad^2H^{10}$ .

### Pyrrhol-red.

$C^{24}N^2H^{14}O^2 = C^{24}Ad^2H^{10}O^2$ .

RUNGE. *Pogg.* 31, 67.

ANDERSON. *Edinb. Phil. Trans.* 21, 4, 571; *Ann. Pharm.* 105, 349; *Chem. Centr.* 1858, 417; *Kopp's Jahresber.* 1857, 398.



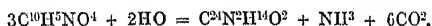
SCHWANERT. *Habilitationschrift, über Zersetzungen der Schleimsäure*, Greifswald, 1860: abstr. *Ann. Pharm.* 116, 279.

First observed by Runge; investigated by Anderson.

*Formation.* 1. Pyrrol is resolved by heat, or by several days' contact with excess of acid, into pyrrol-red and ammonia. (Anderson.)



2. Carbopyrrollic acid, or carbopyrrolate of baryta, is resolved, by heating to  $60^\circ$ , or above, with acids, into carbonic acid and pyrrol, which latter is then decomposed as in 1. (Schwanert.)



Schwanert obtained from carbopyrrolate of baryta 22.05 p. c. carbonic acid, 2.1 nitrogen, as ammonia (calculation, 22.3  $CO^2$ , 2.5 N), but only 22.4 p. c. pyrrol-red (calc. 37.9 p. c.), perhaps because the latter is not always obtained of constant composition.

*Preparation.* Pyrrol is dissolved, with brisk agitation, in oil of vitriol diluted with 4—6 pts. water; the liquid is heated with continued agitation till red flocks separate, then filtered, and immediately washed with boiling water, till nearly all the acid is removed; afterwards with a small quantity of dilute potash-solution. (Anderson.)

*Properties.* Light orange-red powder, which turns brownish when heated. Light or dark brown powder, destitute of taste and odour. (Schwanert.)

Calculation, according to Anderson.				Anderson. mean; in vacuo.	
24 C .....	144	.....	71.28	.....	71.98
2 N .....	28	.....	13.86	.....	13.59
14 H .....	14	.....	6.93	.....	6.88
2 O .....	16	.....	7.93	.....	7.55
<hr/>					
$C^{24}N^2H^{14}O^2$ .....	202	.....	100.00	.....	100.00

Schwanert found in pyrrol-red from carbopyrrollic acid, 59.24 C, 5.94 H, and 62.4 C, 4.7 H, and 11.39 N, after drying at  $110^\circ$ , perhaps because partial decomposition had taken place. (See below).

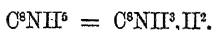
*Decompositions.* After prolonged heating to  $100^\circ$ , it increases in weight from slow oxidation.—2. Yields, by dry distillation, a stinking oil containing pyrrol, and leaves charcoal.—3. Heated in contact with the air, it takes fire and burns away.—4. It is decomposed by prolonged boiling with acids or alkalis, acids converting it into a dark red substance which contains 74 p. c. charcoal. (Anderson.)—5. By nitric acid it is resinised, and afterwards converted into oxalic acid. (Anderson.) Fuming nitric acid dissolves it. (Schwanert.)

Water neither dissolves nor acts on it. It does not dissolve in aqueous acids or alkalis.

Sparingly soluble in cold, more soluble in hot alcohol; sparingly in ether. (Anderson, Schwanert.)

*Appendix to Vol. x., p. 16.*

## Pyrrol.



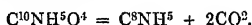
RUNGE. *Pogg.* 31, 67.

ANDERSON. *Ann. Pharm.* 80, 63; *N. Phil. Mag.* J. 2. 457; *Edinb. Phil. Trans.* 20, 2, 247; *J. pr. Chem.* 54, 36; *N. Ann. Chim. Phys.* 34. 332.—*Edinb. Phil. Trans.* 21, 4, 571; *Ann. Pharm.* 105, 349; *Chem. Centr.* 1858, 417; *Kopp's Jahresber.* 1857, 398.

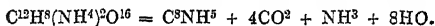
SCHWANERT. *Habilitationschrift über Zersetzungen der Schleimsäure.* Greifswald, 1860; abstr. *Ann. Pharm.* 116, 279.

*Roßhöl.*—Discovered by Runge in 1834, but first prepared pure and investigated by Anderson.

*Formation.* 1. Carbopyrrolic acid is resolved by heat into pyrrol and carbonic acid. (Schwanert.)



2. By the dry distillation of mucate of ammonia. (Schwanert.)



3. In the dry distillation of coal and of various animal matters, passing over, with many other bodies, into coal-tar oil, the wash-water of the illuminating gas, and bone-oil. (Runge, Anderson.) Feathers distilled *per se* yield considerable quantities of pyrrol, together with other bases; flannel also yields it, together with sulphuretted hydrogen, sulphide of carbon, and carbonate of ammonia. (Williams, *Chem. Gaz.*, 1858, 309; *Ann. Pharm.* 109, 127.)—4. By the dry distillation of many organic bases. It is found among the products of distillation of quinine and cinchonine (xiii. 244) and of pelosene, together with methylamine and ethylamine. (Williams, *Chem. Gaz.* 1858, 321; *Rép. Chim. pure.* 1, 118.) Pyrrol is contained in the so-called oil of tobacco. (Runge.)

*Preparation.* 1. *From Mucate of ammonia.* When dry pulverised mucate of ammonia is subjected to dry distillation, crystals of carbonate of ammonia are obtained, together with an aqueous solution of carbopyrrolamide (= bipyromucamide, x. 405,) and a brown oil floating thereon. The latter is washed with water, dehydrated with lumps of potash, distilled, and rectified after standing over chloride of calcium. The greater the quantity of mucate of ammonia heated at once, the larger is the proportion of pyrrol obtained. Carbopyrrolic acid does not yield pure pyrrol so easily, because it sublimes at the same time. (Schwanert.)

2. *From Bone-oil.* Large quantities of crude bone-oil are subjected to fractional distillation; the water which passes over with the first portions is removed; the more volatile half of the oily distillate is mixed with dilute sulphuric acid and set aside for several days; and the strongly acid liquid separated from the undissolved oil is kept

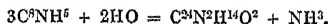
boiling in a still as long as a colourless stinking oil passes over, which soon becomes reddish, and afterwards nearly black, on exposure to the air. The oil, freed from water, is resolved by repeated fractional distillation into several parts. The portion which distils over between  $132^\circ$  and  $143^\circ$  is repeatedly shaken up with a small quantity of very dilute sulphuric acid, to remove admixed picoline; the solutions are separated; and the remaining oil, amounting to about  $\frac{1}{3}$  of the original quantity, is dehydrated with lumps of potash, and rectified, the last portion of the distillate being each time removed, till (after about 15 distillations) nearly the whole passes over between  $134.5^\circ$  and  $138^\circ$ . The pyrrol thus obtained is still contaminated with a small quantity of a substance producing formic and propionic acids, from which it may be freed by boiling with hydrate of potash. Anderson therefore mixes it with 5 or 6 parts of potash-hydrate in coarse lumps, and heats it in a copper flask fitted with a long upright condensing tube, till, as the temperature gradually rises, only a small quantity of liquid evaporates, then replaces the vertical by a condensing tube bent downwards, and distils off all that is volatile at a red heat. On pouring water upon the fused yellowish white residue, pyrrol separates in the form of an oil, which is obtained pure by rectification. (Anderson.)

*Properties.* Transparent, colourless oil, of sp. gr. 1.077, and boiling point  $133^\circ$ . It has an agreeable ethereal odour, resembling that of chloroform, and a pungent taste. (Anderson, Schwanert.) Pyrrol prepared by method 2, and not treated with hydrate of potash, has an unpleasant odour. (Anderson.) Vapour-density = 2.40; before treatment with potash-hydrate, it is 2.50. (Anderson.) The vapour of pyrrol colours fir-wood, moistened with hydrochloric acid, deep purple-red (Runge); pale red at first, then deep carmine-red. (Anderson.) This test will indicate the presence of an extremely small quantity of pyrrol. (Runge, compare *Pogg.* 32, 322.)

				Anderson.		Schwanert.	
				<i>a.</i> ( <i>mean</i> )	<i>b.</i>	<i>a.</i>	<i>b.</i>
8 C .....	48	....	71.64 .....	71.59 ....	71.54 ....	71.67 ....	71.29
N .....	14	....	20.90 .....	.....	.....	19.80 ....	.....
5 H .....	5	....	7.46 .....	7.87 ....	7.77 ....	7.63 ....	7.59
C <sup>2</sup> NH <sup>5</sup> .....	67	....	100.00 .....	.....	.....	99.10 ....	.....

a. Having an offensive odour; not treated with hydrate of potash. (Anderson).—  
a. Obtained from pure mucate of ammonia; b. from carbopyrrollic acid. (Schwanert.)

*Decompositions.* Pyrrol gradually turns brown when exposed to the air.—When heated with excess of acids, it is resolved into ammonia and pyrrol-red. (Anderson.)



By continued boiling, the liquid is decolorised, and the pyrrol-red is further altered. (Anderson).—Pyrrol is rapidly dissolved by *nitric acid*, giving off red vapours, and forming a dark red liquid, and by longer boiling is converted into oxalic acid. Water added to the red solution throws down a resin. (Anderson.) Aqueous pyrrol is coloured deep red by nitric acid. (Runge.) The aqueous solution of hydrochlorate of pyrrol is decomposed by *bichromate of potash*, with formation of a black

precipitate: with *sesquichloride of iron*, it acquires a green and afterwards a black colour; and, when heated with *sulphate of copper*, forms a green solution, and deposits a small quantity of black powder.—From *bichloride of platinum*, cold hydrochlorate of pyrrol throws down first a yellow and after a few minutes a black platiniferous precipitate. (Anderson.)

Pyrrol is nearly insoluble in *water*. It dissolves slowly in aqueous *acids*, but is insoluble in *alkalis*.

*Chloride of Cadmium with Pyrrol*.—On mixing the alcoholic solutions of pyrrol and chloride of cadmium, a white crystalline powder is formed, insoluble in water, easily soluble in hydrochloric acid, and easily decomposed by heating with water and alcohol. (Anderson.)

				Anderson.
16 C.....	96.0	....	23.50	..... 23.25
2 N.....	28.0	....	6.85	
10 H.....	10.0	....	2.44	..... 2.19
3 CdCl .....	274.5	....	67.21	
<hr/>				
2C <sup>8</sup> NH <sup>5</sup> ,3CdCl.....	408.5	....	100.00	

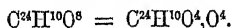
*Mercuric Chloride with Pyrrol*.—Separates on mixing the alcoholic solutions of pyrrol and mercuric chloride, as a white, somewhat crystalline powder, easily altered by excess of mercuric chloride.—It is insoluble in water, sparingly soluble in cold, more easily in boiling alcohol, in the latter, however, with partial decomposition.

				Anderson. mean.
<i>In vacuo.</i>				
8 C .....	48	....	7.88	..... 7.73
N .....	14	....	2.31	
5 H.....	5	....	0.82	..... 0.81
4 Cl.....	142	....	23.31	
4 Hg .....	400	....	65.68	..... 66.89
<hr/>				
C <sup>8</sup> NH <sup>5</sup> ,4HgCl.....	609	....	100.00	

Pyrrol dissolves easily in *alcohol* and *ether*,

*Primary Nucleus* C<sup>24</sup>H<sup>14</sup>; *Oxygen-nucleus* C<sup>24</sup>H<sup>10</sup>O<sup>4</sup>.

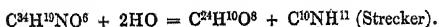
### Piperic Acid.



- VON BABO & KELLER. *Dissertation von C. Keller*, Freiburg, 1856, 16; *Freiburg naturw. Berichte*, 1856; *J. pr. Chem.* 72, 53; *abstr. Chem. Centr.* 1858, 241; *Chem. Gaz.* 1858, 7; *Kopp's Jahresber.* 1857, 413.  
 AD. STRECKER. *Ann. Pharm.* 105, 317; *J. pr. Chem.* 74, 191; *Kopp's Jahresber.* 1857, 415.—*Ann. Pharm.* 118, 280; *N. Ann. Chim. Phys.* 63, 233.  
 G. C. FOSTER. *Chem. Soc. J.* 15, 17.

*Pipericyclic Acid* (Weltzien).

*Formation*. Piperine boiled with alcoholic potash is resolved into piperic acid and piperidine. (v. Babo & Keller.)



*Preparation.* 1 part of piperine is boiled with 3 pts. of potash-hydrate, and 16 to 20 pts. absolute alcohol; the liquid which distils over being continually poured back and the process continued for twelve hours, or till a sample of the mixture taken out of the retort is no longer precipitated by water (Von Babo & Keller); or, better, equal weights of piperine and potash-hydrate, with as much strong alcohol as is required to dissolve both, are heated for 4 or 5 hours to  $100^\circ$  in a closed vessel. (Foster.) The crystalline plates, which are thereby produced in abundance, are separated from the brown mother-liquor, purified by repeated crystallisation from a small quantity of boiling water, with help of animal charcoal, then dissolved in water, and decomposed by dilute hydrochloric acid; and the acid, which separates as a jelly, is collected, washed, and purified by repeated crystallisation from alcohol. Another method is, to neutralise the aqueous solution of the impure potash-salt with acetic acid, mix it with a small quantity of solution of acetate of lead, separate the lead dissolved in the filtered liquid by sulphuretted hydrogen, filter again, and evaporate to the crystallising point (v. Babo & Keller).

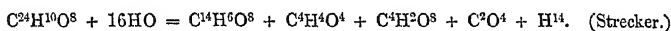
*Properties.* Yellowish capillary needles; in the moist state, sulphur-yellow jelly which shrinks on drying. Melts at  $150^\circ$ , sublimes at about  $200^\circ$ , partly unaltered, emitting an odour of coumarin, and leaving a brown fused residue. Reaction scarcely acid. (v. Babo & Keller.)

				v. Babo & Keller.		Strecker. <i>mean.</i>		Foster.					
<i>at 100°.</i>													
24 C .....	144	....	66.06	....	66.08	to	66.88	....	65.90	....	65.83	....	66.01
10 H .....	10	....	4.59	....	4.80	....	5.14	....	4.65	....	4.92	....	4.94
8 O .....	64	....	29.35	....	29.12	....	27.98	....	29.45	....	29.25	....	29.05
C <sup>24</sup> H <sup>10</sup> O <sup>8</sup> ....	218	....	100.00	....	100.00	....	100.00	....	100.00	....	100.00	....	100.00

This is the formula proposed by Strecker; v. Babo & Keller give the formulæ  $C^{50}H^{22}O^{16}$  and  $C^{50}H^{24}O^{16}$ .

*Decompositions.* 1. For the decomposition by dry distillation, see above.—2. Burns when heated in contact with the air, emitting an odour of anise, and leaving a difficultly combustible charcoal.—3. *Nascent hydrogen* (sodium-amalgam) converts it into hydro-piperic acid (p. 11.) (Foster.)—4. *Oil of vitriol* colours it blood-red, and then chars it.—5. When treated with *iodine, bromine, or chlorine*, it forms substitution-products.—6. Concentrated *hydriodic acid* acts upon it, even below  $100^\circ$ , producing carbonic acid, and a black, uncrystallisable, humus-like substance. (Foster.)—7. In contact with *pentachloride of phosphorus*, it acquires a vermilion-red colour, and deliquesces after a few days, forming oxychloride of phosphorus, and yielding vermilion-coloured crystals. If the product (the crystals, Kr.) obtained by the action of pentachloride of phosphorus on piperic acid is mixed with piperidine, a substance is formed which is insoluble in water and potash-ley, but soluble in strong hydrochloric acid, alcohol, and ether.—8. *Nitric acid*, even when dilute, converts piperic acid into an orange-coloured nitro-compound, which, when heated with potash-hydrate, gives off an odour of coumarin. (v. Babo & Keller.)—¶ 9. Piperic acid added to *fused potash-hydrate* containing a little water in excess, is at first dissolved; immediately afterwards the mixture turns brown, and hydrogen

is evolved, so that the continued addition of piperic acid causes it to froth over if not constantly stirred. When the evolution of gas is no longer perceptible, the mass contains protococatechuic acid, acetate, oxalate, and carbonate of potash, with a relatively small quantity of a humus-like body, probably a product of the decomposition of protococatechuic acid. The reaction which takes place is probably:—



Protocatechuic acid is apparently identical with the acid of the same composition produced by the action of hydriodic acid on hemipinic acid (xiv. 431) ¶.

*Combinations.* Piperic acid is nearly insoluble in *water*. (v. Babo & Keller.) It unites with salifiable bases, forming the *piperates*, which according to Strecker, are composed of  $\text{C}^{24}\text{H}^9\text{MO}^8$ , but according to v. Babo & Keller, are bimetallic salts, containing  $\text{C}^{50}\text{H}^{22}\text{M}^2\text{O}^{16}$ , or  $\text{C}^{50}\text{H}^{20}\text{M}^2\text{O}^{16}$ .

*Piperate of Ammonia.*—Piperic acid is added to hot concentrated ammonia, as long as it continues to dissolve; the filtrate is left to cool, and the resulting crystals are dried, first over a mixture of lime and sal-ammoniac, then over oil of vitriol.—Colourless scales, with satiny lustre, resembling cholesterin. When exposed in the moist state to the air, it gives off ammonia, and turns yellow. Between  $100^\circ$  and  $150^\circ$ , it gives off ammonia, without further alteration and without loss of water; and between  $180^\circ$  and  $200^\circ$ , it decomposes, emitting an odour of anise. (v. Babo & Keller.)

<i>at 50° in vacuo.</i>				<i>v. Babo &amp; Keller.</i>	
24 C.....	144	....	61.28	.....	61.77
N .....	14	....	5.95	.....	5.73
13 H .....	13	....	5.53	.....	6.17
8 O .....	64	....	27.24	.....	26.33
$\text{C}^{24}\text{H}^9(\text{NH}^4)\text{O}^8$ .....				235	.... 100.00
				.....	100.00

*Piperate of Potash.*—Obtained as already described (p. 8), or by dissolving the acid in potash-ley. Yellowish-white, silky laminæ, probably belonging to the right prismatic system. When heated, it glows and emits an odour of anise, and when subjected to dry distillation, yields a small quantity of tar, containing carbolic acid, and leaves a mixture of charcoal and carbonate of potash. It dissolves sparingly in cold, easily in boiling water, sparingly in alcohol, and is nearly insoluble in ether. (v. Babo & Keller.)

<i>v. Babo &amp; Keller.</i>				<i>Foster.</i>	
<i>mean.</i>				<i>(at 100°).</i>	
24 C.....	144.0	....	56.21	....	55.73
9 H.....	9.0	....	3.51	....	3.63
7 O.....	56.0	....	21.86	....	22.75
KO .....	47.2	....	18.42	....	17.89
$\text{C}^{24}\text{H}^9\text{KO}^8$ .....				256.2	.... 100.00
				....	100.00
				....	100.00
				....	100.00

*Piperate of Soda.*—Precipitated on dissolving the acid in hot soda-ley, and cooling, as a white crystalline powder sparingly soluble in cold, easily in hot water, and precipitated from the aqueous solution by alcohol,

A concentrated solution of chloride of potassium, containing only 2 per cent. of chloride of sodium, still yields a precipitate of this salt, when treated with piperate of potash. (v. Babo & Keller.)

*Piperate of Baryta.*—Obtained as a loosely coherent, white precipitate, by treating the aqueous solution of the potash-salt with chloride of barium. Microscopic needles, requiring about 5000 pts. of water to dissolve them, and undergoing partial decomposition at the same time (v. Babo & Keller); more soluble in hot water. (Foster.)

	at 100°.	v. Babo & Keller.		Foster.
		mean.		(at 100°).
24 C .....	144 ....	50.43 ....	51.05	
9 H .....	9 ....	3.15 ....	3.78	
7 O .....	56 ....	19.63 ....	18.85	
BaO .....	76.6 ....	26.79 ....	26.32 ....	26.77 .....
$C^{24}H^{10}BaO^8$ .....	285.6 ....	100.00 ....	100.00	

The salt is completely decomposed by a stream of carbonic acid passed through its boiling aqueous solution. (Foster.)

*Piperate of Strontia.*—White precipitate, obtained by adding a strontia salt to the aqueous potash-salt (v. Babo & Keller).

*Piperate of Lime.*—Aqueous piperate of potash added to a solution of chloride of calcium, throws down slender needles, somewhat more soluble in water than the baryta-salt. It contains 50.07 to 52.62 per cent. C, 3.96 to 4.10 H, and 12.03 lime. (v. Babo & Keller.)

*Piperate of Magnesia.*—Moderately dilute solutions of piperate of potash and hydrochlorate of magnesia deposit this salt, after a few days, in long slender needles. (v. Babo & Keller.)

From salts of *alumina*, piperate of potash throws down a white precipitate.

*Piperate of Manganese.*—Small, yellowish laminæ, having a silky lustre. (v. Babo & Keller.)

*Piperate of Zinc.*—Yellowish white, curdy precipitate, obtained by precipitating chloride of zinc with the potash-salt. (v. Babo & Keller.)

*Piperate of Cadmium* is a white powder. The *lead-salt* is a yellowish precipitate, which dissolves slightly when heated, and separates as a white crystalline powder on cooling. — *Ferrous piperate* is yellowish white, insoluble, easily oxidisable. — *Piperate of cobalt* is rose-coloured; *piperate of nickel* light green, insoluble. (v. Babo & Keller.)

*Piperate of Copper* is precipitated by the potash-salt from sulphate of copper, more abundantly on addition of ammonia, in slender sky-blue needles. Contains 49.67 C, 3.68 H, 15.36 O, and 31.29 p.c.  $CuO$ . (v. Babo & Keller.)

*Mercurous Piperate.*—White precipitate, reduced by ammonia. (v. Babo & Keller.)

*Mercuric Piperate.*—Yellowish white precipitate, from which potash-ley separates mercuric oxide. (v. Babo & Keller.)

*Piperate of Silver.*—Obtained as a colourless, scarcely crystalline powder, by precipitating nitrate of silver with the aqueous potash-salt. Insoluble in water and alcohol. (v. Babo & Keller.) Does not diminish in weight at 100°. (Strecker.)

		at 100°.		v. Babo & Keller.		Strecker.	
				mean.		mean.	
24 C	..... 144	....	44.31	....	43.42	.....	44.35
9 H	..... 9	....	2.76	....	3.01	.....	2.85
8 O	..... 64	....	19.69	....	20.52	.....	19.65
Ag	..... 108	....	33.24	....	33.05	.....	33.15
<hr/>							
C <sup>24</sup> H <sup>9</sup> O <sup>8</sup>	..... 325	....	100.00	...	100.00	.....	100.00

When *terchloride of gold* is mixed with piperate of potash, a yellowish white precipitate is obtained, which soon yields metallic gold. (v. Babo & Keller.)

*Piperate of Piperidine.*—(p. 14.)

Piperic acid dissolves in 270 pts. of absolute *alcohol*, easily in the same liquid at the boiling heat. It dissolves but sparingly in *ether*, either hot or cold, scarcely at all in *sulphide of carbon* or *rock-oil*; somewhat more easily in *benzene*. (v. Babo & Keller.)

#### Appendix to Piperic acid.

#### ¶ Hydropiperic Acid.



G. C. FOSTER (1862). *Chem. Soc. J.* 15, 19; abstr. *Zeitschr. Ch. Pharm.* 5, 9; and *Private communication*.

*Formation and Preparation.* An aqueous solution of piperate of potash is treated with sodium-amalgam, at a gentle heat; after the action has been continued for some hours, the addition of hydrochloric acid precipitates hydropiperic acid in oily drops, which gradually solidify on standing. It may be purified by crystallisation from a large quantity of boiling water, or by solution in alcohol and treatment with animal charcoal.

*Properties.* Colourless; tasteless at first, after a time somewhat burning. As deposited from boiling water, it forms long, exceedingly thin, silky needles; by the spontaneous evaporation of its ethereal solution, it may be obtained in tolerably large, hard crystals, apparently monoclinic (oblique prismatic), and mostly hemitropic. Melts at 63° or 64°; solidifies at about 56°; not volatile without decomposition.

						Foster.	
24 C	..... 144	....	65.46	....	65.24	....	65.44
12 H	..... 12	....	5.45	....	5.65	....	5.67
8 O	..... 64	....	29.09	....	29.11	....	28.89
<hr/>							
C <sup>24</sup> H <sup>12</sup> O <sup>8</sup>	..... 220	....	100.00	....	100.00	....	100.00



*Decompositions.* 1. When *heated* somewhat above its melting point, it gives off choking white fumes, which, when diluted with much air, smell like oil of anise, and leaves a small, easily combustible, carbonaceous residue.—2. Strong *hydriodic acid* decomposes it, below  $100^\circ$ , into carbonic acid and a black humus-like body, which gives a black solution with alkalis.—3. *Fuming nitric acid* colours it blood-red; *ordinary nitric acid*, diluted with its own bulk of water, acts violently upon it if gently heated, giving a solution from which water precipitates a semi-fluid nitro-acid.—4. *Oil of vitriol* colours it blood-red.—5. Fused with excess of *hydrated alkali*, it evolves much gas, and the brown fused mass exhibits the reactions of the acid  $C^{14}H^6O^8$ , obtained by the action of hydriodic acid on hemipinic acid (xiv. 431; see also *Decompositions of piperic acid*, xv. 8)—6. With *chloride of acetyl* at  $150^\circ$ , it yields hydrochloric acid and a neutral oil, insoluble in water and dilute alkalis.

*Combinations.* With *water*. Hydripiperic acid is very slightly soluble in cold water, somewhat more so in hot water; the hot saturated solution reacts strongly acid; on cooling, it deposits the acid in oily drops, as long as its temperature is above the melting point of the latter; the rest separates in long, thin crystals (vid. sup.).

With *salifiable bases*, it forms *hydropiperates*, salts containing  $C^{24}H^{11}MO^8$ .

*Hydropiperate of Ammonia* crystallises from hot water in small shining scales.

Foster.							
$C^{24}H^{15}O^8$ .....	220	....	92.83	....	92.85	....	93.01
$NH^3$ .....	17	....	7.17	....	6.55	....	7.16
<hr/>							
$C^{24}NH^{15}O^8$ .....	237	....	100.00	....	99.40	....	100.17

Easily soluble in *hot water*, considerably less soluble in cold. A strong aqueous solution can dissolve more *hydropiperic acid*, forming a solution from which water precipitates the excess of acid, and which gives, if saturated, an almost solid mass of hydropiperate of ammonia, on the addition of strong aqueous ammonia.

*Hydropiperate of Potash with excess of acid.*—Obtained by boiling a solution of hydropiperic acid in nearly absolute alcohol, with dry carbonate of potash. Crystallises on cooling in hemispherical masses of radiating needles.

Foster. (at $100^\circ$ .)							
48 C .....	288	....	60.25	.....	59.38		
23 H .....	23	....	4.81	.....	5.11		
K .....	39	....	8.16	.....	8.59		
16 O .....	128	....	26.78	.....	26.92		
<hr/>							
$C^{48}H^{23}KO^{16}$ .....	478	....	100.00	.....	100.00		

Decomposed into neutral hydropiperate of potash and hydropiperic acid, completely by solution in water, partially by solution in alcohol.

*Hydropiperate of Baryta.*—Crystallises from boiling water in small bunches of needle-shaped crystals. The formula  $C^{24}H^{11}BaO^8$  requires 23.8 p. c. barium; Foster found 23.2 p. c.

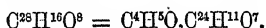
*Hydropiperate of Lime.* — Prepared by boiling the acid with milk of lime, filtering hot, and separating the excess of lime by carbonic acid; or by precipitating a rather strong solution of the ammonia-salt with chloride of calcium. Purified by crystallisation from a mixture of 2 parts water and 1 pt. alcohol. Small needle-shaped crystals. Slightly soluble in cold water, more soluble in hot water, but partially decomposed by it. The crystals contain water, which they lose at 100°. The formula  $C^{24}H^{11}CaO^8$  requires 8.37 p. c. calcium; Foster found 8.35 and 8.30 p. c.

*Hydropiperate of Silver.* — Crystalline precipitate, almost insoluble in cold water; easily altered by exposure to light, or by solution in hot water. The formula  $C^{24}H^{11}AgO^8$  requires 33.03 p. c. silver; Foster found 33.58 p. c.

The hydropiperates of the other heavy metallic oxides are mostly precipitates insoluble in cold water.

Hydropiperic acid dissolves in all proportions in *alcohol*, and is very soluble in *ether*.

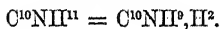
### Hydropiperate of Ethyl.



*Formation and Preparation.* By heating a solution of hydropiperic acid in absolute alcohol saturated with hydrochloric acid for 4 or 5 hours to 130° in a sealed tube. Purified by solution in ether and treatment with animal charcoal. Brownish yellow, neutral liquid; heavier than, and insoluble in, water. Not altered by dilute aqueous potash or ammonia. Decomposed by gaseous ammonia, probably with formation of *hydropiperamide*. (Foster.) ¶.

*Appendix to Vol. x., p. 446.*

### Piperidine.



WERTHEIM. *Ann. Pharm.* 70, 58.

ANDERSON. *Ann. Pharm.* 75, 82; *Compt. rend.* 31, 126; *Ann. Pharm.* 84, 345; *Compt. rend.* 34, 564; *Lieb. Kopp's Jahresber.* 1852, 545.

CAHOURS. *Compt. rend.* 34, 481; *Instit.* 1852, 98; *J. pr. Chem.* 56, 203; *Ann. Pharm.* 84, 342; *Chem. Gaz.* 1852, 167. In full: *N. Ann. Chim. Phys.* 38, 76; abstr. *Lieb. Kopp's Jahresber.* 1852, 546.

VON BABO & KELLER. *J. pr. Chem.* 72, 53; abstr. *Chem. Centr.* 1858, 241; *Chem. Gaz.* 1858, 7; *Kopp's Jahresber.* 1857, 413.

The production of a volatile base by heating piperine with soda-lime was first noticed by Wertheim and Rochleder, who at first mistook

it for aniline (*Ann. Pharm.* 54, 255); afterwards for picoline (*ibid.* 70, 58).—Anderson and Cahours obtained the same base independently of each other, and recognised its separate identity: its chemical relations were investigated chiefly by Cahours.

The greater part of the results obtained by Anderson and Cahours have already been detailed (x. 446). We here give the remainder, together with those of Wertheim and of v. Babo & Keller.

According to Wertheim's latest statements (*Gerh. Traité*, 4, 98), the volatile base obtained by heating piperine with potash-lime is  $C^{12}NH^{13}$ , inasmuch as he found in its platinum-salt, 23·11—23·86 C, 4·71—4·54 H and 32·49 Pt (calc.  $C^{12}NH^{13}, HCl, PtCl^2 = 23·56$  C, 4·58 H, and 32·41 Pt.)

*Formation and Preparation.* Piperine is decomposed, as directed at page 8, by boiling with alcoholic potash, into piperidine and piperate of potash, and the mother-liquor separated from the crystals of that salt is distilled into a receiver containing hydrochloric acid, whereby hydrochlorate of piperidine is obtained. (v. Babo & Keller.)

Piperidine forms with *chlorine* or *bromine*, an oily product, not possessing basic properties. (For the other reactions, see x. 447.)

*Chloro-aurate of Piperidine.*—Hydrochlorate of piperidine forms, with terchloride of gold, small needles of a fine yellow colour. (Cahours.)

*Piperidine with Protochloride of Platinum.*—Protochloride of platinum acts violently on piperidine, forming the compound  $C^{10}NH^{11}, PtCl$ . The solution of this salt in a large quantity of boiling water, deposits, on evaporation, the piperidine-compound corresponding to Magnus's green ammonio-protochloride of platinum. (Williams, *Chem. Gaz.* 1858, 346; *J. pr Chem.* 76, 251.)

*Chloroplatinate of Piperidine.*—( $C^{10}NH^{11}, HCl, PtCl^2$ , according to Cahours (x. 449);  $C^{12}NH^{13}, HCl, PtCl^2$ , according to Wertheim (p. 14). This last formula is very doubtful.

*Piperate of Piperidine.*—Obtained by dissolving piperic acid in aqueous piperidine, as a crystalline pulp, and on dilution, in colourless laminae, having a silky lustre. In contact with the air or with oil of vitriol, it turns yellow from loss of piperidine. Melts at 100° without further alteration, and when strongly heated, gives off piperidine and decomposes. When heated for some time to 150°, it becomes partially insoluble in water, but if then dissolved in an alkali, yields unaltered piperic acid when decomposed by acids. With pentachloride of phosphorus, it behaves like piperic acid. Contains 26·75 per cent. piperidine. (v. Babo & Keller.) Calc. 28·05 per cent.

<i>Dried over oil of vitriol.</i>				<i>v. Babo &amp; Keller.</i>	
34 C.....	204	....	67·32	.....	66·11
N.....	14	....	4·62	.....	
21 H.....	21	....	6·93	.....	7·29
8 O.....	64	....	21·13	.....	
$C^{24}H^{10}O^8, C^{10}NH^{11}$ .....				303	.... 100·00

It had lost a portion of its piperidine. (v. Babo & Keller.)

Piperidine coagulates *white of egg* after a quarter of an hour. (Wertheim.)

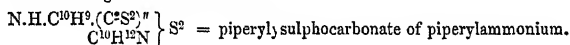
*Conjugated Compounds of Piperidine.*

**Piperidine with Sulphide of Carbon  $C^{22}N^2H^{22}S^4$ .**

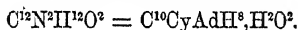
*Pipéryl-sulfocarbonate de pipéridine.* (Gerhardt, *Traité* 4, 105.) *Sulfocarbonyl-Pipipéryl-Sulfbiaminsäure.* (Weltzien *Syst.* 23.)

This compound, discovered by Cahours (x. 448), is obtained by carefully dropping sulphide of carbon into piperidine, and crystallising the product from alcohol. It forms slender needles belonging to the oblique prismatic system. (Fig. 100.) Rhombic prism  $u$ , having the oblique terminal face  $i$ , resting on its obtuse lateral edge. The obtuse edges formed by  $i$  and  $u$  are truncated by the octahedral faces  $\alpha$ ;  $u : u$  in front =  $116^\circ 4$ ; on the side =  $63^\circ 56$ ;  $i : u$  above  $\alpha = 96^\circ 52'$ ;  $\alpha : u = 141^\circ 6'$ ;  $\alpha : i = 135^\circ 46$ , calculated. (De Sénarmont, *N. Ann. Chim. Phys.* 34, 89.)

Gerhardt assigned to it the formula—



**Piperidine-urea.**



CAHOURS. *N. Ann. Chim. Phys.* 38, 84.

*Pipéryl-urea, Urée pipéridique.*

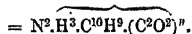
*Formation.* 1. From cyanic acid vapour and piperidine.—2. From dissolved sulphate of piperidine and cyanate of potash.—3. From moist chloride of cyanogen and piperidine.

*Preparation.* A mixture of the solutions of sulphate of piperidine and cyanate of potash, in equivalent proportions, is boiled down to dryness, and the residue is exhausted with strong alcohol. The alcoholic solution left to evaporate freely, yields crystals of the compound urea.

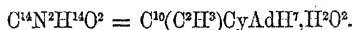
*Properties.* Long white needles.

				Cahours.
12 C .....	72	...	56.25	..... 56.32
2 N .....	28	...	21.87	..... 22.05
12 H .....	12	...	9.37	..... 9.41
2 O .....	16	...	12.51	..... 12.22
<hr/>				
$C^{22}N^2H^{12}O^2$ .....	128	...	100.00	..... 100.00

May be regarded as carbamide in which 1 At. H is replaced by pipéryl,—



Soluble in water and in alcohol.

**Methyl-piperidine-urea.**

CAHOURS. *N. Ann. Chim. Phys.* 38, 85.

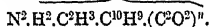
*Methyl-piperyl-urea. Methylurée pipéridique.*

Piperidine becomes intensely hot when vapour of cyanate of methyl is passed into it, and solidifies on cooling. The mass is purified by pressure and recrystallisation from boiling alcohol.

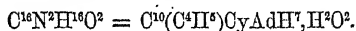
Long needles having a strong lustre.

	<i>Fused.</i>			<i>Cahours.</i>	
14 C .....	84	....	59·15	.....	58·91
2 N .....	28	....	19·71	.....	19·52
14 H .....	14	....	9·86	.....	10·04
2 O .....	16	....	11·28	.....	11·53
<hr/>					
$\text{C}^{14}\text{N}^2\text{H}^{14}\text{O}^2$ .....	142	....	100·00	.....	100·00

Carbamide in which 1 At. H is replaced by methyl and another by piperyl,—



Dissolves easily in boiling *alcohol*.

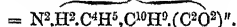
**Ethyl-piperidine-urea.**

CAHOURS. *N. Ann. Chim. Phys.* 38, 86.

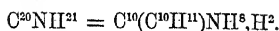
Obtained similarly to methyl-piperidine-urea, by the action of cyanate of ethyl on piperidine. Resembles the preceding.

				<i>Cahours.</i>	
				<i>mean.</i>	
16 C .....	96	....	61·54	.....	61·54
2 N .....	28	....	17·94	.....	18·13
16 H .....	16	....	10·26	.....	10·22
2 O .....	16	....	10·26	.....	10·11
<hr/>					
$\text{C}^{16}\text{N}^2\text{H}^{16}\text{O}^2$ .....	156	....	100·00	.....	100·00

Carbamide, in which 1 At. H is replaced by ethyl and another by piperyl,—



*Methyl-piperidine.*  $\text{C}^{10}\text{N}(\text{C}^2\text{H}^3)\text{H}^{10}$  and *Ethyl-piperidine.*  $\text{C}^{10}\text{N}(\text{C}^4\text{H}^5)\text{H}^{10}$ .  
(see vol. x, pp. 449, 451.)

**Amyl-piperidine.**

CAHOURS. *N. Ann. Chim. Phys.* 38, 95.

*Mylepiperidine.*

Piperidine is heated with iodide of amyl in the water-bath for several days; the resulting crystalline mass is dissolved in a small quantity of water, and distilled with lumps of caustic potash. The oily distillate is dried with fused hydrate of potash, and rectified.

Colourless oil, boiling at  $186^\circ$ , and smelling like ammonia and fusel-oil. Vapour-density = 5.477.

Cahours.						Vol.	Density.
20 C	120	...	77.41	...	77.54	C-vapour	8.3200
N	14	...	9.04	...	9.17	N-gas	0.9706
21 H	21	...	13.55	...	13.63	H-gas	1.4553
<hr/>							
$\text{C}^{20}\text{NH}^{21}$	155	...	100.00	...	100.34	Vapour of $\text{C}^{20}\text{NH}^{21}$	10.7459
						1	5.3729

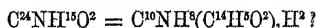
Less soluble in *water* than methyl- or ethyl-piperidine.  
Forms crystallisable salts with most *acids*.

*Hydriodate of Amyl-piperidine.*—Broad, white, shining laminae.

Cahours.					
20 C	120	...	42.55	...	42.26
N	14	...	4.96	...	5.12
22 H	22	...	7.80	...	7.74
I	126	...	44.69	...	
<hr/>					
$\text{C}^{20}\text{NH}^{21}, \text{HI}$	282	...	100.00	...	

*Chloroplatinate of Amyl-piperidine.*—Bichloride of platinum separates, from the warm solution of hydrochlorate of amyl-piperidine, dark orange-yellow oil-drops, which, after a few hours, solidify in the crystalline form. From solution in moderately warm dilute alcohol, the compound crystallises in very hard prisms of a fine orange-red colour.

Cahours.					
20 C	120.0	...	33.28	...	33.13
N	14.0	...	3.87	...	
22 H	22.0	...	6.10	...	6.23
3 Cl	106.5	...	29.54	...	
Pt	98.0	...	27.21	...	27.39
<hr/>					
$\text{C}^{20}\text{NH}^{21}, \text{HCl}, \text{PtCl}_2$	360.5	...	100.00	...	

**Benzopiperide.**

CAHOURS. *N. Ann. Chim. Phys.* 38, 88.

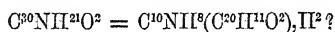
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C

By treating piperidine with chloride of benzoyl, a heavy oil is obtained which, when treated with acidulated water, yields hydrochlorate of piperidine, while benzoyl-piperide remains undissolved, and quickly solidifies; it is purified by recrystallisation from alcohol.—Beautiful colourless prisms.

					Cahours. mean.
24 C .....	144	...	76.19	.....	75.91
N .....	14	...	7.41	.....	7.57
15 H .....	15	...	7.94	.....	8.11
2 O .....	16	...	8.46	.....	8.41
<hr/>					
$C^{24}NH^{16}O^2$ .....	189	...	100.00	..	100.00

### Cumylpiperide.



CAHOURS. *N. Ann. Chim. Phys.* 38, 88.

Obtained like the preceding, by the action of chloride of cumyl on piperidine.—Beautiful tabular crystals.

					Cahours.
30 C .....	180	...	77.92	.....	78.05
N .....	14	...	6.06	.....	
21 H .....	21	...	9.09	.....	9.18
2 O .....	16	...	6.93	.....	
<hr/>					
$C^{30}H^{21}NO^2$ .....	231	...	100.00		

### Conjugated Compounds of Piperic Acid.

#### Piperine.



- OERSTED (1819). *Schw.* 29, 80; *J. Phys.* 90, 173.  
 PELLETIER. *Ann. Chim. Phys.* 16, 344; *Schw.* 32, 435; *Ann. Chim. Phys.* 51, 199; *Schw.* 67, 93; *Ann. Pharm.* 6, 33.  
 MERCK. *N. Tr.* 20, 1, 34.  
 WACKENRODER. *Br. Arch.* 37, 349.  
 DUFLOS. *Schw.* 61, 220.  
 VARRENTTRAPP & WILL. *Ann. Pharm.* 39, 283.  
 TH. WERTHEIM. *Ann. Pharm.* 70, 58; *Pharm. Centr.* 1849, 520; *N. J. Pharm.* 17, 65; *Compt. Chim.* 1849, 375; *Lieb. Kopp. Jahresber.* 1849, 378.  
 GERHARDT. *Compt. Chim.* 1849, 375; *Lieb. Kopp. Jahresber.* 1849, 379; *Rev. Scient.* 10, 201; *N. Ann. Chim. Phys.* 7, 253.  
 ANDERSON. *Ann. Pharm.* 75, 82; *Compt. rend.* 31, 136; *Ann. Pharm.* 84, 345; *Lieb. Kopp. Jahresber.* 1852, 545.

CAHOURS. *Compt. rend.* 34, 481; *J. pr. Chem.* 56, 203; *Ann. Pharm.* 84, 342; *Chem. Gaz.* 1852, 167.—In detail: *N. Ann. Chim. Phys.* 38, 76.

STENHOUSE. *Ann. Pharm.* 95, 106.

V. BABO & E. KELLER. *Dissert. von E. Keller*, Freiburg, 1856, 16; *J. pr. Chem.* 72, 53; *abstr. Chem. Centr.* 1858, 541; *Chem. Gaz.* 1858, 7; *Kopp's Jahresber.* 1857, 413.

A. STRECKER. *Ann. Pharm.* 105, 317; *J. pr. Chem.* 74, 191; *Kopp's Jahresber.* 1857, 415.

Discovered by Oersted in 1819.

*Source.* In black and long pepper.—In black pepper from Western Africa, *Cubeba Glusii*, which does not contain any cubebin. (Stenhouse.)

*Preparation.* 1. Coarsely pulverised pepper is exhausted with cold water; the residual powder repeatedly digested with alcohol of 80 per cent.; the alcohol distilled off from the tinctures; the residue evaporated to an extract, and this extract, after standing for several days, washed with cold water. The undissolved residue is then dissolved in alcohol; a quantity of hydrate of lime is added, equal to  $\frac{1}{8}$  of the pepper used; and the liquid, filtered after a day's digestion, is left to crystallise. The resulting crystals, if impure, may be purified by trituration, washing with ether, and recrystallisation from alcohol, with help of animal charcoal. (Wittstein.)—Vogel (*Br. Arch.* 26, 294) first recommended the washing of the pepper with water; Pfeil (*Mag. Pharm.* 13, 56) and Hoff (*Repert.* 25, 400) the use of hydrate of lime. Henkenius (*Mag. Pharm.* 13, 59) proceeds in a similar manner. The piperine thus obtained amounts to 2.4 p. c. of the pepper.

2. White pepper is exhausted with alcohol of sp. gr. 0.833; the tincture is distilled to an extract; and this extract is mixed with potash-ley, which dissolves the resin and leaves a green powder. The latter is washed with water, dissolved in alcohol of sp. gr. 0.833 and crystallised. By repeated crystallisation the piperine is obtained colourless. (Pontet, *J. Chim. Méd.* 1, 531; *Berzel. Lehrb.* 3 Aufl. 7, 577.)—This method is preferred by Pelletier and Berzelius. See also Buchner (*Repert.* 22, 270); Carpenter, *Sill. Am. J.* 13, 334; Meli (*Brugn. Giorn.* 17, 76).—Stenhouse dissolves the extract of cubebs, prepared with wood-spirit, in alcohol, and mixes it with strong potash-ley, whereupon a brown oil separates, which yields crystals on standing. The mother-liquor, if again mixed with alcohol, yields another portion of oil, which likewise deposits crystals on standing. These crystals are purified by pressure and recrystallisation.

3. Winckler distils the alcohol from the alcoholic tincture of long pepper; dissolves the residue in the required quantity of hot alcohol; precipitates the solution with basic acetate of lead; mixes the filtrate while warm with as much sulphuric acid as is necessary to precipitate the lead; filters while warm; distils the alcohol from the filtrate; exhausts the residue with water; and dissolves the undissolved portion in hot alcohol, whereupon piperine crystallises on cooling. (*Mag. Pharm.* 18, 153.)

Impure piperine may be purified by washing with absolute alcohol, or better with weak potash-ley. (Henry & Plisson.)



*Properties.* Colourless, vitreous, flattened, four-sided, obliquely truncated prisms. (Pelletier.) Rhombic prisms, with lateral angles of 95 and 85°. (Gmelin.) Oblique rhombic prisms, with angles of 92° 45' and 87° 15'. The terminal face is obliquely set on the obtuse lateral edge, with angles of 106° 30' and 73° 30'. (Wackenroder.) Rhomboidal prisms, with angles of 85° 40' and 94° 20'. (Regnault.) — Kopp (*Einleitung in die Krystallographie*, s. 312,) describes rhombic prisms of 84° 30', the acutely set terminal face making an angle of 75° 50' with the prism. — Rhombic prism, having its base set obliquely upon the obtuse lateral edge; the acute lateral edges often truncated. Fig. 85, without  $\alpha$  and  $f$ ;  $u : u = 84^\circ 42'$ ;  $i : u$  (behind) =  $75^\circ 30' 32''$ . (Dauber, *Ann. Pharm.* 74, 204.) — Crystals belonging to the oblique prismatic system. Fig. 87 without  $\alpha$ . Rhombic prism,  $u : u$  (in front) =  $95^\circ 22'$ ; on the edge truncated by  $t$ , therefore,  $u : u = 84^\circ 38'$ ;  $u : h = 120^\circ 42'$ ;  $u$  behind,  $75^\circ 45'$ , in front  $104^\circ 15'$ .  $i : h = 135^\circ 3'$ ;  $h : h = 121^\circ 13'$ . It is only in very small crystals that the angles of the rhombic prisms can be measured. In larger crystals the faces are curved, and the edges imperfectly developed. The octahedral faces  $h$  were developed only in one of the crystals examined. Haidinger states, however, that truncations of the combination-edge  $i : u$  above and in front by the other half of the octahedron (Fig. 100,  $\alpha$ ) likewise occur. — The crystals have an imperfectly vitreous, sometimes fatty, lustre. Colour of the crystals examined, greenish yellow, or lemon-yellow. Transparent to semi-transparent; trichromatic. With the dichroscopic lens, the following tints are observed: Perpendicular to  $i$ : nearly colourless, brightest tint; colour of the axis  $b$  which unites the faces  $t$ : yellow, comparatively light; that of the axis  $\alpha$  (parallel to  $i$ ): yellow, comparatively dark. (Schabus, *Bestimmung d. Krystallgest.* p. 177.)

Piperine melts at about 100° (Pelletier); at 110° or above (Wackenroder) to a pale yellow limpid oil, which solidifies on cooling to a pale yellow, transparent, strongly refracting resin (Gmelin, Wackenroder). Sp. gr. of fused piperine 1.1931 at 18°. (Wackenroder.) Nearly tasteless by itself (Vogel), but has a sharp peppery taste when dissolved in alcohol. Impure piperine has a sharp taste, even by itself. It has no alkaline reaction. (Pelletier.) Its solution does not deflect the plane of polarisation of light. (Bouchardat, *N. Ann. Chim. Phys.* 9, 227.)

				Liebig.	Pelletier.	Regnault. <i>mean.</i>		
34 C	.....	204	....	71.58	.....	69.47	....	71.19
N	.....	14	....	4.91	.....	4.09	....	4.94
19 H	.....	19	....	6.67	.....	6.69	....	6.78
6 O	.....	48	....	16.84	.....	19.44	..	17.09
<hr/>								
C <sup>34</sup> NH <sup>19</sup> O <sup>6</sup>	....	285	....	100.00	.....	100.00	....	100.00
<hr/>								
				Gerhardt. <i>mean.</i>	Laurent.	Stenhouse. <i>mean.</i>		
C	.....			71.52	.....	71.66	.....	71.72
N	.....			4.81	.....		.....	4.76
H	.....			6.68	.....	6.66	.....	6.66
O	.....			16.99	.....		.....	16.86
<hr/>								
				100.00				100.00

Will & Varrentrapp found 4.56 p. c. N.

Regnault (*Ann. Chim. Phys.* 68, 158) first gave the correct formula, which was

corroborated by Laurent (*Ann. Chim. Phys.* 19, 363), and finally settled by Strecker's investigation. Older formulæ:  $C^{40}NH^{24}O^8$  (Pelletier);  $C^{40}NH^{22}O^8$  (Liebig, *Ann. Pharm.* 6, 36);  $C^{70}N^2H^{38}O^{12}$  (Gerhardt);  $C^{70}N^2H^{39}O^{12}$  (Wertheim);  $C^{70}N^2H^{40}O^{12}$  (v. Babo & Keller). Compare also O. Henry & Plisson (*J. Pharm.* 17, 449).

*Decompositions.* 1. Piperine blackens by *dry distillation*, and yields a brown empyreumatic oil, from which carbonate of ammonia crystallises. (Gmelin.)—2. *Heated* in a platinum spoon, it melts like wax, takes fire at a stronger heat, and leaves an easily combustible charcoal. (Merck.)—3. Piperine suspended in acidulated water and exposed to the action of the *electric current*, is violently attacked, as also by hot concentrated nitric acid. (Hlasiwetz & Rochleder, *Wien. Akad. Ber.* 5, 447.)—4. It is coloured blood-red by *oil of vitriol*, loses this colour on addition of water, and, if the action of the oil of vitriol has not been continued for a very long time, does not appear to be sensibly altered. (Pelletier.) Oil of vitriol dissolves part of the piperine with the same colour, and water precipitates it in flocks. (Dulong, *J. Pharm.* 11, 52.) The solution becomes black on standing. (Wackenroder.) See also Duflos (*Schw.* 61, 220.) This solution in oil of vitriol, on being mixed with bichromate of potash, gives off gases, and assumes a brownish green colour, finally changing to dirty green; peroxide of lead colours it dirty brown-red, and ultimately black. (Riegel *N. Br. Arch.* 58, 293). Compare also Eboli (*N. Br. Arch.* 85, 186.)—5. *Bromine* converts piperine into a peculiar, non-crystalline product. (Gerhardt.)—6. *Iodine* acts upon it only when the two are fused together, forming a dark black-brown mass, which hardens on cooling. (Wackenroder.)—7. *Nitric acid* colours piperine greenish yellow, orange, and then red; dissolves it with a yellow colour, the solution yielding dirty yellow flakes when mixed with water, and, on further action, produces oxalic acid, together with a yellow artificial bitter. (Pelletier, Oersted, Wackenroder.) Strong nitric acid forms an orange-red resin, which partly dissolves with deepening colour when heated. The solution no longer yields piperine when treated with water or alkalis. (Duflos.) The brown resin which is produced from piperine by nitric acid, with violent action, evolution of nitrous acid, and the odour of bitter almond-oil, assumes a splendid blood-red colour when treated with hydrate of potash, and when boiled therewith, yields a distillate of piperidine. (Anderson.) Von Babo & Keller, by treating piperine with *nitrous acid*, and subsequently distilling it with potash-ley, obtained volatile needles which had the odour of cumarin, melted in boiling water, dissolved in alcohol and ether, and, after fusion with hydrate of potash, gave the reaction of salicylic acid with sesquichloride of iron.

8. By boiling with *alcoholic potash*, piperine is converted into piperidine and piperate of potash. (v. Babo & Keller).  $C^{34}NH^{19}O^8 + KO, HO = C^{34}KH^{19}O^8 + C^{10}NH^{11}$ . (Strecker, *Ann. Pharm.* 105, 317.) When heated with *potash-lime* it yields a volatile base (Wertheim, see page 13; also x. 446) piperidine. (Cahours.) The distillate contains water, two volatile bases, the piperidine constituting the chief portion, and traces of a neutral body having an aromatic odour like that of benzoin. (Cahours.) If the mixture is heated in the oil-bath, not above  $160^\circ$ , no ammonia is produced, and there remains a brown mass, which hardens on cooling. If this be pulverised, washed successively with cold water and alcohol to remove hydrate of potash and undecomposed piperine, then repeatedly digested with hot dilute hydrochloric acid, and the resulting resinous cake dissolved in alcohol, water separates from the solution, yellow flocks, which, after drying in *vacuo*, contain on the average

78.36 p. c. C., 6.96 H., 4.08 N., and 15.10 O., which Wertheim represents by the formula  $C^{128}N^3H^{67}O^{20}$ . When piperine is heated with soda-lime to a temperature above  $200^{\circ}$ , a larger quantity of piperidine is obtained, together with ammonia, and the residue if supersaturated with hydrochloric acid, deposits yellow flocks containing 71.41 p. c. C., 5.65 H., and 22.94 O., according to Wertheim =  $C^{58}H^{27}O^{14}$ . Piperine heated with *hydrate of potash*, melts, gives off a sharp odour of pepper, and yields a milky aqueous distillate. When more strongly heated, it gives off hydrogen gas with intumescence, and finally ammonia. (Gerhardt.)—9. Heated with *bichromate of potash* and dilute sulphuric acid, it gives off a large quantity of carbonic acid, and yields a slightly acid aqueous distillate which reduces nitrate of silver. The residue smells like bitter almonds, and when evaporated to dryness and exhausted, first with alcohol, then with water, leaves a greenish amorphous extract. (Gerhardt.)—10. *Pernanganate of potash* added to a solution of piperine mixed with sulphuric acid, colours it green after a few hours. (Duflos.)

*Combinations.* Piperine is insoluble or very sparingly soluble in cold water, slightly in hot water, whence it is deposited on cooling. (Pelletier, Oersted.)

It is not perceptibly soluble in aqueous *mineral acids*; neither does it combine with them. (Pelletier, Dulong, Regnault.)

Piperine combines with *iodine*, forming shining, bluish black needles, soluble in alcohol, and containing  $C^{68}N^2H^{38}O^{12}I^3$ . (see Weltzien, *Syst. Zusammenst.* 562.)

*With Hydrochloric acid.* Fuming hydrochloric acid colours piperine deep yellow, itself acquiring the same colour by contact with it. (Pelletier, Dulong.) The solution of piperine in alcoholic hydrochloric acid leaves, when evaporated in vacuo, a residue free from hydrochloric acid. (Regnault.) When dry hydrochloric acid is passed over air-dried piperine, ultimately heated to fusion, the mass acquires a lemon-yellow colour, changing to light brown, and takes up 13.05 to 13.74 p. c. HCl, without separation of water. ( $C^{34}NH^{19}O^9 \cdot HCl = 12.63$  p. c. HCl.) The transparent mass solidifies in the crystalline form on cooling, is decomposed by water into piperine and aqueous hydrochloric acid, and dissolves in alcohol. (Varrentrapp & Will.)

From solution in *perchloric acid*, piperine crystallises out unaltered by spontaneous evaporation. (J. Büdecker, *Ann. Pharm.* 71, 63.)

Piperine does not dissolve in aqueous *ammonia* or in the fixed *alkalis*. (Merck.)

*Phosphomolybdic acid* colours piperine brown-yellow, and precipitates it in flocks. (Sonnenschein, *Ann. Pharm.* 104, 45.) Piperine likewise forms a yellow precipitate with a very dilute solution of *phosphantimonic acid* (the acid mixture obtained by dropping pentachloride of antimony into aqueous phosphoric acid.) (Schultze, *Ann. Pharm.* 109, 179.)

*Piperine with Chloride of Cadmium.*—Straw-yellow needles containing  $C^{68}N^2Li^{36}(O)^{12} \cdot 2HCl, 9CdCl + 6H_2O$ . (Galletly, *N. Edinb. Phil. J.* 4, 94; *Chem. Centr.* 1856, 606.)

With a very dilute solution of *potassio-mercuric iodide*, piperine forms a yellowish white, permanently amorphous precipitate. (Dell's *N. Jahrb. Pharm.* 2, 31.)

*Chloromercurate of Piperine* is obtained by mixing a solution of 1 pt.

piperine in strong alcohol acidulated with hydrochloric acid, with an alcoholic solution of 2 pts. mercuric chloride, collecting the crystals after three days, and washing them with alcohol. Yellow, shining, transparent crystals which become darker by exposure to the air, or at the heat of the water-bath. They belong to the doubly oblique prismatic system. The crystals consist of three hexaïd faces  $y, z, u$  (*fig. u*), the edge between  $y$  and  $u$ , to the right above, being truncated by a dodecaïd face  $g$ ; the edge between  $u$  and  $z$ , to the left in front, truncated by three dodecaïd faces  $v, v^1, v^2$  (in the figure  $v$  and  $v^2$  would come between  $v$  and  $z$ ); the edge between  $z$  and  $u$  truncated by a dodecaïd face  $w$ ; the edge between  $z$  and  $y$ , to the front above, truncated by a decaïd face  $t$ ; the edge between  $y$  and  $z$ , to the front below, truncated by a dodecaïd face  $t'$ ; and the summit between  $u, v, y$ , to the right above, truncated by an octaïd face  $o$ .— $z : u = 102^\circ 51'$ ;  $z : w = 144^\circ 35'$ ;  $w : u = 138^\circ 16'$  (by calculation)  $= 138^\circ 18'$  (by observation);  $y : w = 119^\circ 9'$ ;  $z : v = 133^\circ 31'$ ;  $u$  (left) :  $v = 123^\circ 37'$ ;  $y : v = 106^\circ 51'$ ;  $w : v$  over  $z = 98^\circ 6'$ ;  $z : v = 169^\circ 58'$  (calculated)  $= 170^\circ 8'$  (observed);  $u$  (left) :  $v^1 = 87^\circ 10'$  (calculated)  $= 87^\circ 4'$  (observed);  $y : v^1 = 120^\circ 4'$ ;  $v : v^1 = 143^\circ 33'$ ;  $z : v^2 = 178^\circ 28'$ ;  $u$  (left) :  $v^2 = 101^\circ 20'$ ;  $y : u$  over  $g = 102^\circ 24'$ ;  $g : y = 147^\circ 35'$ ;  $g : u = 134^\circ 49'$ ;  $g : z = 120^\circ 18'$  (calculated)  $= 120^\circ 20'$  (observed);  $y : c = 121^\circ 46'$ ;  $t : z = 111^\circ 52'$ ;  $t : u = 91^\circ 22'$ ;  $t : y = 126^\circ 21'$ ;  $t : y = 123^\circ 51'$ ;  $o : z$  (behind)  $= 98^\circ 17'$  (calculated)  $= 98^\circ 15'$  (observed);  $o : u = 130^\circ 19'$ ;  $o : y = 125^\circ 59'$ ;  $o : v$  behind  $= 125^\circ 75'$ ;  $o : w = 141^\circ 25'$ ;  $o : t = 141^\circ 3'$ . The faces  $v^1$  and  $v^2$  occur but rarely. The crystals are short prisms in the direction of  $z$  and  $u$ . They are plane and smooth faced,  $u$  only being sometimes curved. Lustre vitreous, somewhat fatty and adamantine. Transparent to semi-transparent. Slightly trichromatic. Powder lemon-yellow. (Schabus, *Bestimmung*, p. 198.)

Insoluble in water, sparingly soluble in strong hydrochloric acid and in cold alcohol, more easily in hot alcohol. (Hinterberger, *Wien. Akad. Ber.* 6, 114; *Ann. Pharm.* 77, 204; *J. pr. Chem.* 53, 246).

				Hinterberger.
				mean.
68 C.....	408.0	....	46.49	..... 46.75
2 N .....	28.0	....	3.19	.....
39 H .....	39.0	....	4.44	..... 4.49
12 O .....	96.0	....	10.94	.....
2 Hg.....	200.0	....	22.79	..... 22.35
3 Cl .....	106.5	....	12.15	.....
<hr/> 2C <sup>34</sup> NH <sup>19</sup> O <sup>6</sup> , HCl, 2HgCl....				8:7.5 .... 100.00

According to Hinterberger it is C<sup>70</sup>N<sup>2</sup>H<sup>37</sup>O<sup>10</sup>, HCl, 2HgCl + 2H<sub>2</sub>O.

When an alcoholic solution of hydrochlorate of piperine mixed with alcoholic cyanide of mercury is left to evaporate in the air, a reddish yellow resin is obtained, together with free piperine.

*Chloroplatinate of Piperine*.—First observed by Varrentrapp & Will.—A concentrated alcoholic solution of piperine is mixed with concentrated alcoholic bichloride of platinum and fuming hydrochloric acid, the mixture is left to evaporate, and the resulting crystals are washed with strong alcohol. Large aurora-red crystals belonging to the oblique prismatic system. Taste sharp and burning. Unalterable at 100°, melts somewhat above 100°, and decomposes with strong tune-

faction (Wertheim.) Dissolves very sparingly in water, being resolved at the same time into hydrochloric acid and piperine [and bichloride of platinum]. (Varrentrapp & Will; Wertheim.) Dissolves in cold alcohol, and very abundantly in hot alcohol, so that on cooling, a large quantity of a fiery orange-yellow powder is precipitated. (Wertheim.)

						Wertheim. mean.
68 C	.....	403.0	....	52.54	.....	54.52
2 N	.....	28.0	....	3.60	.....	3.53
39 H	.....	39.0	....	5.02	.....	5.30
12 O	.....	96.0	....	12.43	.....	10.54
Pt	.....	98.7	....	12.71	.....	12.70
3 Cl	.....	106.5	....	13.70	....	13.41
<hr/>						
$2C^{24}NH^{10}O^6, HCl, PtCl^2$						776.2 .... 100.00 ..... 100.00

Wertheim's formula  $C^{70}N^2H^{37}O^{10}, HCl, PtCO^2$  agrees better with his analysis, but it assigns to free piperine, the formula  $C^{70}N^2H^{37}O^{10}$  or  $C^{70}N^2H^{37}O^{10} + 2HO$ , which is not at all probable.

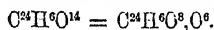
Piperine dissolves readily in *acetic acid*; the solution is precipitated by water, and yields feathery crystals by evaporation. (Pelletier, Merck.)

It dissolves more readily in hot *alcohol* than in cold, and is precipitated by water. (Pelletier.) Soluble in 30 pts. of cold, and in an equal quantity of boiling alcohol. (Wittstein.) The solution is rendered milky by water, and deposits the piperine in small crystals. (Wackenroder.)

Piperine dissolves in 60 pts. of *ether* (Merck), in 100 pts. of cold, and in a smaller quantity of warm ether. It dissolves in *volatile oils*, and crystallises as the solvent evaporates. (Pelletier.) It dissolves abundantly in warm *creosote*, and remains dissolved on cooling. (Reichenbach.)

*Oxygen-nucleus*  $C^{24}H^6O^8$ .

### Glaucomelanic Acid.



WÖHLER & MERKLEIN. *Ann. Pharm.* 55, 129.

Known only as a potash-salt.

*Formation.* 1. By the action of the air on ellagic acid in presence of excess of alkali. — 2. On mixing ellagate of potash with hypochlorite of potash.

*Preparation of Glaucomelenate of Potash.* — Ellagic acid is dissolved in cooled, moderately strong potash-ley, and left to stand in contact with the air, whereupon the solution first assumes a deep reddish yellow colour, then becomes lighter, and, commencing from the surface, deposits glaucomelenate of potash in slender black crystals, intermingled with ellagate, if the solution has stood for too long a time in contact with air containing carbonic acid. The liquid is decanted before the separation of ellagate of potash begins, and the black crystalline powder is washed, first with water containing potash, then with pure water. Glaucomelenate of soda may also be obtained by heating ellagic acid with soda-ley; but it is more difficult to purify.

*Properties of the Potash-salt.* — Blue-back, crystalline, shining powder, appearing under a magnifying power of 200, to consist of broad, thin prisms, black-blue by transmitted light. The air-dried salt gives off in vacuo  $\frac{3}{4}$  of its crystallisation-water, and the rest at 100° without further alteration, the total quantity being on the average 16·84 p. c. (calc. 4 at. HO = 17·53 p. c.)

	at 120°.		Wöhler & Merk'lein.	
24 C .....	144·0	42·55	40·95	41·72
4 H .....	4·0	1·18	0·98	1·29
12 O .....	96·0	28·38	29·38	30·16
2 KO .....	94·4	27·89	28·68	26·83
<hr/>				
C <sup>24</sup> K <sup>2</sup> H <sup>4</sup> O <sup>14</sup> .....	338·4	100·00	100·00	100·00

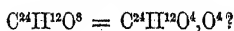
The reproduction of ellagic acid from glaucomelanin acid makes the formula of the latter appear doubtful. (Gerhardt, *Traité* 3, 873.)

*Decompositions.* 1. Glaucomelanate of potash when heated in a tube, gives off water, carbonises, without yielding any empyreumatic products, and leaves charcoal, together with carbonate of potash. — 2. It dissolves abundantly in hot water and in contact with the air, with green, and afterwards with yellow, colour, forming ellagate of potash, which separates from the solution on cooling. If the potash-salt be heated with water, and evaporated to dryness, a dirty olive-green mass is obtained, equal in weight to the original salt. The latter yields 73 p. c. of brownish ellagic acid, and a quantity of chloride of potassium equivalent to 29 pts. of potash. — 3. Heated with hydrochloric acid, it yields a deposit of ellagic acid. — 4. With nitrous acid vapour, it assumes a fine purple-red colour. — 5. In hot concentrated potash-ley it dissolves with deep emerald-green colour, quickly changing to deep yellow in contact with the air.

The acid dissolves sparingly in cold water, with blackish purple colour. It is insoluble in alcohol.

Primary Nucleus C<sup>24</sup>H<sup>16</sup>: Oxygen-nucleus C<sup>24</sup>H<sup>12</sup>O<sup>4</sup>.

### Filpelosic Acid.



LUCK. *Jahrb. pr. Pharm.* 22, 139 and 141.

#### Filimelistic acid.

*Preparation.* 1. Filicic acid (from *Aspidium filix mas*, see below) is dissolved in warm, very dilute potash-ley; the solution exposed to the air for a week; and the filtrate precipitated with dilute sulphuric acid. The precipitate is washed, dried and obtained as a loosely coherent powder, by solution in ether-alcohol and spontaneous evaporation of the filtrate. — 2. When filicic acid is heated with dilute alcoholic ammonia to 80° or 100° for some time out of contact with the air, the liquid then precipitated with sulphuric acid, and the precipitate purified as in 1, Luck's filimelistic acid is obtained.

*Properties.* Amorphous loam-coloured powder; when prepared by 2, it consists of microscopic spherules. Tasteless.

<i>In vacuo.</i>					Luck. <i>mean.</i> a.	<i>In vacuo.</i>					Luck. <i>mean.</i> b.			
24 C	...	144	...	65.45	...	64.92	24 C	.....	144	...	62.88	...	62.81	
12 H	...	12	...	5.45	...	6.16	13 H	.....	13	...	5.67	...	5.71	
8 O	...	64	...	29.10	...	28.92	9 O	.....	72	...	31.45	..	31.48	
C <sup>24</sup> H <sup>12</sup> O <sup>8</sup> 220					...	100.00	C <sup>24</sup> H <sup>12</sup> O <sup>8</sup> .HO 229					...	100.00	...

Luck regards the acids obtained by 1 and 2 as different, the former as  $C^{24}H^{13}O^8$ , the latter as  $C^{24}H^{13}O^9$ , although they agree perfectly in their properties, and in the composition of their lead-salts. The formulæ given by Luck for chloro- and bichloro-filipelosic acid, as well as that of filimelisi-sulphuric acid are improbable in the highest degree. (Kr.)

Filipelosic acid melts and burns when heated on platinum-foil. — It is converted by dry chlorine into chlorofilipelosic acid; by aqueous chlorine into bichlorofilipelosic acid.

It is insoluble in water, but dissolves with brown colour in oil of vitriol. It dissolves readily in aqueous alkalis; the solution yielding with most metallic salts, precipitates varying in colour from yellow to brown.

*Lead-salt.* Precipitated from the soda-salt by neutral acetate of lead.

<i>In vacuo.</i>					Luck.				
					a.	b.			
24 C	.....	144	....	42.23	.....	40.32	....	41.15	....
13 H	.....	13	....	3.81	.....	4.07	....	4.06	....
9 O	.....	72	....	21.11	.....	21.91	....	22.83	....
PbO	.....	112	....	32.85	.....	33.70	....	31.96	....
$C^{24}H^{12}PbO^8, 2HO$ 341					....	100.00	....	100.00	....

a is Luck's filipelosate of lead; b his filimelisate.

Filipelosic acid dissolves in sulphide of carbon, alcohol, ether, volatile oils and fixed oils.

### Filimelisi-sulphuric Acid.

LUCK. *Jahrb. pr. Pharm.* 22, 149.

*Preparation.* Filicic acid is triturated with 6 or 8 pts. of fuming oil of vitriol till completely dissolved; the solution after standing for 2 to 4 hours, is dropped into a dilute and cooled solution of Glauber's salt, avoiding all rise of temperature; and the precipitate is collected, washed with cold solution of Glauber salt, to remove free acid, then pressed and dried. The dry mass treated with warm alcohol or ether, yields up its acid to the solvent, while sulphate of soda remains behind; the acid may then be obtained in the solid state by evaporating the filtrate.

Transparent, amorphous, brown-yellow mass, which may be

rubbed to a gold-yellow powder. Inodorous. Tastes bitter. Has a faint acid reaction.

				Luck. mean.
24 C .....	144	...	55.17	55.32
13 H .....	13	...	4.98	5.29
8 O .....	64	...	24.49	23.90
SO <sup>3</sup> .....	40	...	15.36	15.19
<hr/>				
C <sup>24</sup> H <sup>13</sup> O <sup>8</sup> ,SO <sup>3</sup> .....	261	...	100.00	100.00

After deduction of a certain amount of ash.—So, according to Luck; but the formula is not in accordance with the principles of this Handbook.

Insoluble in *water*; dissolves with deep yellow colour in *alkalis*. The solution of the baryta-salt precipitates metallic salts brown, but not nitrate of silver.

*Baryta-salt*.—Prepared by mixing the aqueous acid with baryta-water, and removing the excess of baryta by passing carbonic acid through the liquid, evaporating, and redissolving as long as carbonate of baryta continues to separate.—Amorphous mass, having a fine red-lead colour, and bitter taste; easily soluble in water.

Calculation according to Luck.				Luck.
24 C .....	144	...	42.66	42.35
13 H .....	13	...	3.85	3.90
8 O .....	64	...	18.96	
SO <sup>3</sup> .....	40	...	11.85	
BaO .....	76.5	...	22.68	23.07
<hr/>				
C <sup>24</sup> H <sup>13</sup> O <sup>8</sup> ,SO <sup>3</sup> ,BaO .....	337.5	...	100.00	

*Lead-salts. a. Mono-acid*.—Yellowish red precipitate, obtained by mixing the aqueous baryta-salt with neutral acetate of lead.

				Luck.
24 C .....	144	...	38.61	38.34
13 H .....	13	...	3.48	3.57
8 O .....	64	...	17.15	
SO <sup>3</sup> .....	40	...	10.72	
PbO .....	112	...	30.04	29.32
<hr/>				
C <sup>24</sup> H <sup>13</sup> O <sup>8</sup> ,SO <sup>3</sup> ,PbO .....	373	...	100.00	

*b. With excess of Lead-oxide*.—Brick-red precipitate, obtained by adding neutral acetate of lead to the aqueous solution of the baryta-salt mixed with ammonia. A precipitate of the same colour is obtained by treating the aqueous baryta-salt with basic acetate of lead.

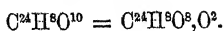
				Luck.
24 C .....	144	...	20.31	20.10
13 H .....	13	...	1.83	1.87
8 O .....	64	...	9.02	
SO <sup>3</sup> .....	40	...	5.64	
4PbO .....	448	...	63.20	63.49
<hr/>				
C <sup>24</sup> H <sup>13</sup> O <sup>8</sup> ,SO <sup>3</sup> ,4PbO.....	709	...	100.00	

The acid dissolves readily in *alcohol* and in *ether*.



Oxygen-nucleus  $C^{24}H^8O^8$ .

### Luteolin.



CHEVREUL. (1830). *J. Chim. Méd.* 6, 157; *Berz. Jahresber.* 11, 280.

MOLDENHAUER. *Ann. Pharm.* 100, 180; *Dingl. polyt. J.* 144, 71; *J. pr. Chem.* 70, 478.

SCHÜTZENBERGER & PARAF. *Compt. rend.* 52, 92; *Zeitschr. Ch. Pharm.* 4, 134.

Discovered by Chevreul. — Different from Liesching's luteolin, a preparation from weld, which is used in dyeing. (*Comp. Chem. Centr.* 1856, 159.)

*Occurrence.* In dyer's weld. (*Reseda luteola.*)

*Preparation.* Weld is exhausted with hot alcohol of 80 per cent.; the tinctures are concentrated by distilling off the alcohol, and by further evaporation; and the impure luteolin which separates after standing for a day is collected. For purification, either the luteolin is dissolved in boiling concentrated vinegar, the solution evaporated, and the luteolin extracted from the residue by ether (containing water); or the separated impure luteolin is dried, washed several times with a small quantity of ether, which chiefly takes up resin, and dissolved in a larger quantity of ether. The whole of the luteolin thus prepared may be obtained pure and crystallised, by pouring the solution into 20 times its volume of water, then boiling, filtering, and cooling the filtrate. (Moldenhauer.) The alcoholic extract of weld may likewise be dissolved in alcohol, the alcohol distilled off, and the luteolin precipitated from the hot-filtered residue by neutral acetate of lead. The precipitate is decomposed under water by sulphuretted hydrogen, the sulphide of lead collected and dried, the adhering luteolin extracted therefrom by ether containing water, and then re-crystallised from alcohol. It may also be re-crystallised from dilute sulphuric acid, acetic acid of 15 to 20 per cent., or water with 2 per cent. alcohol. (Moldenhauer).—2. Weld is exhausted with alcohol; the alcoholic solution precipitated with water, and the precipitate heated with water to  $250^\circ$  in a closed steel cylinder. After cooling, the sides of the cylinder are found to be coated with crystals, which must be separated from the cake of resin at the bottom, and purified by two crystallisations from over-heated water. (Schützenberger & Paraf.)

By precipitating the aqueous decoction of weld with basic acetate of lead (or agitating it with hydrated oxide of lead), decomposing the washed precipitate with sulphuretted hydrogen, and evaporating the filtrate in vacuo, Preisser (*1 ev. scient.* 16, 56; *J. pr. Chem.*) obtained his luteolin in white spangles, slightly acid, and of sweetish bitter taste. This product sublimes in golden yellow needles, and, by exposure to the air or by boiling with chromic acid, is converted into broad gold-yellow spangles, Preisser's *luteolein*. It dissolves in water, is coloured bright yellow and afterwards precipitated by ammonia or the fixed alkalis, likewise by lime-, strontia-, or baryta-water. From a solution of neutral acetate of lead, it throws down a white precipitate, which becomes gold-yellow on exposure to the air, and from ferrous sulphate, a pale greenish-yellow precipitate, which turns brown when exposed to the air. It dissolves in alcohol and ether. (Since, however, Preisser's other statements respecting colouring matters have been often refuted, it is probable that these also are not deserving of much confidence. Kr.).

Compare, on this subject, Arppe, *Ann. Pharm.* 55, 101; Schlieper, *Ann. Pharm.* 58, 369; Schiel, *Ann. Pharm.* 60, 76; Bolley, *Ann. Pharm.* 62, 150; Weyermann & Haffely, *Ann. Pharm.* 74, 226; Elsner, *J. pr. Chem.* 35, 377; Bolley & Wydler, *J. pr. Chem.* 43, 507; Wagner, *J. pr. Chem.* 51, 82).

*Properties.* Small four-sided needles, of pure yellow colour, and silky lustre. It sometimes separates from ether in the amorphous state (Moldenhauer.) Inodorous, but tastes slightly bitter and harsh. Melts above  $320^{\circ}$ , with partial decomposition. Slightly acid. (Moldenhauer.) Air-dried luteolin contains 10.23 p. c. water (3 at. = 10.42 p. c.), after drying over oil of vitriol 7.02 p. c. (2 at. = 7.2 p. c.) which goes off at  $150^{\circ}$ . (Schützenberger & Paraf.)

Calculation according to :

1.			2.			3.		
Schützenberger & Paraf.			Moldenhauer.			Hlasiwetz.		
24 C .....	144 ...	62.07	40 C .....	240 ....	62.92	58 C .....	348 ....	62.14
8 H .....	8 ....	3.45	14 H .....	14 ....	3.66	20 H .....	20 ....	3.37
10 O .....	80 ....	34.48	16 O .....	128 ....	33.52	24 O .....	192 ....	34.29
$C^{24}H^8O^{10}$ ...	232 ....	100.00	$C^{40}H^{14}O^{16}$ ...	382 ....	100.00	$C^{58}H^{20}O^{24}$ ...	560 ....	100.00

Moldenhauer. at $100^{\circ}$ .			Schützenberger & Paraf. at $150^{\circ}$ .		
C .....	62.50 to	63.00	.....	61.67 to	62.54
H .....	3.70 „	4.08	.....	3.49 „	3.77
O .....	33.80 „	32.92	.....	34.84 „	33.69
100.00 to 100.00			.....	100.00 to 100.00	

Moldenhauer analysed luteolin re-crystallised from sulphuric acid, acetic acid or alcohol, with nearly equal results. From his determinations of the quantities of metal in the luteolin-salts, he regards the formula as not completely established. According to Hlasiwetz (*Ann. Pharm.* 112, 107), luteolin might be identical with alpha-quer-cetrin (calculation 3); this however is doubted by Bolley. (*Ann. Pharm.* 115, 60.)

*Decompositions.* 1. By *anhydrous phosphoric acid* at  $200^{\circ}$ , luteolin is converted into a red substance, which dissolves with violet colour in ammonia (Schützenberger & Paraf.)—2. When luteolin is heated with *caustic ammonia* to  $100^{\circ}$  in a closed tube for three or four days, a deep yellow solution is formed, which, when evaporated, leaves a dark-coloured substance, whence ammonia is evolved by hydrate of potash, but not by lime: probably luteolamide. (Schützenberger & Paraf.)—3. With warm concentrated *nitric acid*, it turns red-brown and partially dissolves, the solution depositing brown flocks when mixed with water. By longer boiling, a colourless solution is formed containing oxalic acid.—4. By distillation with *chromic acid*, it yields formic acid. (Moldenhauer.)—5. From *nitrate of silver* it reduces the metal without previous reddening. (Bolley.)

Luteolin dissolves in 14,000 pts. of cold and 5,000 pts. of boiling water, and is precipitated in the amorphous state by acids. (Moldenhauer.) According to Chevreul, it dissolves very easily in water. Dissolves in *oil of vitriol*, with deep reddish-yellow colour, and is precipitated by water without alteration. Dissolves sparingly in dilute acids. (Moldenhauer.) According to Chevreul, it unites with acids.

Luteolin unites with *bases*. (Chevreul.) It dissolves in aqueous ammonia with deep yellow colour, and remains behind free from ammonia when the solution is evaporated. (Moldenhauer.)

*Luteolin with Potash*.—Prepared from luteolin and carbonate of potash, similarly to alizarin-soda (xiv, 139), and contains 29·3 p. c. potash, (Moldenhauer.) ( $C^{24}H^8O^{10}$ , 2 KO = 28·92 p. c. KO [Kr.]) With aqueous alkalis, luteolin forms gold-yellow solutions, which undergo slow alteration on exposure to the air. (Chevreul.)

*Luteolin with Baryta*.—Produced by mixing a hot aqueous solution of luteolin with caustic baryta, then with one-third of its volume of alcohol (Moldenhauer.)

*Luteolin with Oxide of Lead*.—A hot aqueous solution of luteolin forms, with alcoholic acetate of lead, a beautiful yellow precipitate, containing 46·12 p. c. PbO. (Moldenhauer.) Alcoholic acetate of lead precipitates alcoholic luteolin. (Schützenberger & Paraf.)

Schützenberger & Paraf.					
24 C .....	144	....	31·44	.....	30·97
8 H .....	8	....	1·75	.....	1·98
10 O .....	80	....	17·90	.....	17·72
2 PbO .....	224	....	48·91	.....	49·33
<hr/>					
$C^{24}H^8O^{10}$ , 2PbO.....	456	....	100·00	.....	100·00

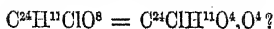
Aqueous luteolin does not affect *ferrous* salts, but colours a very dilute solution of *ferric chloride* green at first but afterwards red-brown, the latter colour being produced immediately in more concentrated solutions. (Moldenhauer, Bolley.)

A compound of luteolin with *cupric oxide*, is formed by precipitating the hot aqueous solution with sulphate of copper; it has a dark colour, and contains 20·16 p. c., CuO. (Moldenhauer.)

Luteolin dissolves in 37 pts. of *alcohol* and 6·25 pts. *ether*. It dissolves with peculiar facility in strong warm *acetic acid*, and separates almost completely on cooling. It does not precipitate a solution of gelatin. Its warm aqueous solution imparts a fine jonquil-yellow colour, after some time to silk and wool mordanted with alum, and olive-green to the same fabrics mordanted with iron. (Chevreul.)

### *Oxychlorine-nucleus* $C^{24}ClH^{11}O^4$ .

### Chlorofilipelosic Acid.



LUCK. *Jahrb. pr. Pharm.* 22, 144.

When dry chlorine gas is passed over filipelosic acid in a bulb-tube, the acid melts, with rise of temperature and evolution of hydrochloric acid gas, to a transparent light-brown mass, which, after washing with water, dissolves in ether-alcohol with dark brown-yellow colour, and remains behind when the alcohol is left to evaporate.

Amorphous, transparent, light-brown mass, which may be rubbed to a brown powder, has a faint fruity odour, a slightly bitter taste, and strong acid reaction.

				Luck.
24 C .....	144.0	....	54.68	..... 54.59
12 H .....	12.0	....	4.55	..... 4.78
Cl .....	35.5	....	13.48	..... 13.50
9 O .....	72.0	....	27.29	..... 27.13
<hr/>				
$C^{24}H^{11}ClO^8, HO$ ....	263.5	....	100.00	..... 100.00

According to Luck it is  $C^{24}H^{12}ClO^9$  (see page 26).

*Potash-ley* colours the acid dark brown, probably forming chloride of potassium.

The acid is insoluble in water, but dissolves with brown-yellow colour in *alkaline liquids*. The alcoholic solution of the soda-salt forms brown-yellow precipitates with most metallic salts, but darkens the solution of nitrate of silver without precipitating it.

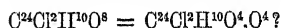
*Lead-salt*.—By precipitating the dilute aqueous soda-salt with neutral acetate of lead.

				Luck.
	<i>In vacuo.</i>			
24 C .....	144.0	....	38.40	..... 38.30
12 H .....	12.0	....	3.20	..... 3.22
Cl .....	35.5	....	9.45	
9 O .....	72.0	....	19.20	
PbO .....	112.0	....	29.75	..... 29.31
<hr/>				
$C^{24}H^{10}ClO^7, PbO + 2HO$ ....	375.5	....	100.00	

The acid dissolves in *alcohol*, more readily in *ether*, less easily in *sulphide of carbon*, *fixed oils*, and *oil of turpentine*.

*Oxychlorine-nucleus*  $C^{24}Cl^2H^{10}O^4$ .

### Bichlorofilpelosic Acid.



Luck. *Jahrb. pr. Pharm.* 22, 146.

Chlorine is passed into water in which filpelosic acid is suspended, as long as the odour of the gas disappears after the liquid has been left to itself for a while; the product is then washed with water, and purified by solution in alcohol and spontaneous evaporation.

Amorphous mass, which may be rubbed to a light brown powder, and melts at a gentle heat. Tasteless. Has an acid reaction.

				Luck.
	<i>In vacuo.</i>			
24 C .....	144	....	46.93	..... 46.68
12 H .....	12	....	3.91	..... 4.09
2 Cl .....	71	....	23.08	..... 23.44
10 O .....	80	....	26.08	..... 25.79
<hr/>				
$C^{24}Cl^2H^{10}O^8, 2HO$ ....	307	....	100.00	..... 100.00

According to Luck it is  $C^{24}Cl^2H^{10}O^{10}$  (comp. p. 26.)

Insoluble in *water*, but dissolves in aqueous *alkalis*, forming salts

which precipitate the solutions of metallic salts, like chloroflupelosate of soda.

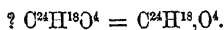
*Lead-salt.* — Obtained like the lead-salt of the monochlorinated acid.

	<i>In vacuo.</i>		Luck.	
24 C .....	144	27.64	27.42	
11 H .....	11	2.11	2.15	
2 Cl .....	71	13.63		
9 O .....	72	13.79		
2 PbO .....	224	42.83	42.95	
<hr/>				
$C^{24}CPH^9PbO^8, PbO, 2HO$ ....	522	100.00		

The acid dissolves in *alcohol* and in *ether*, sparingly in *sulphide of carbon*, *fixed oils*, and *oil of turpentine*.

*Primary Nucleus*  $C^{24}H^{18}$ .

### Kinovous Acid.



KAWALIER. *Wien. Akad. Ber.* 11, 344. — 13, 525.

*Quinovous acid.* *Chinovigesäure.*

*Occurrence.* In the needles of *Pinus sylvestris*. In the green parts of *Thuja occidentalis*.

*Preparation.* 1. *From Pine-needles.* The needles are cut up and boiled with alcohol of  $40^\circ$ ; the alcoholic decoction is distilled in the water-bath, the greater part of the volatile oil then passing over with the alcohol; and the distillate is mixed with water. It is thereby separated into a dark green resinous mass containing ceropic acid, kinovous acid, and a small quantity of volatile oil, and a turbid watery liquid in which pinipicrin, sugar, traces of citric acid, oxypinotanic acid and pinitannic acid remain dissolved. The needles exhausted with alcohol still contain a little pinipicrin and jelly, which latter may be obtained in the manner described at page 239, vol. xiii. The resinous mass is dissolved in alcohol of  $40^\circ$ ; an alcoholic solution of neutral acetate of lead added, which throws down impure ceropate of lead (to be treated as described under ceropic acid); sulphuretted hydrogen is passed into the filtrate; and the precipitated mixture of chlorophyll and sulphide of lead is separated by filtration. The now yellow filtrate deposits, after the alcohol has been distilled off, a semi-fluid resin, which dissolves in very dilute potash-ley, to a light brown liquid, from which the *resins* may be precipitated in combination with lime by chloride of calcium. These resins are filtered off and washed with water, and the filtrate and wash-water are precipitated with a slight excess of hydrochloric acid, whereby faintly yellow flocks of kinovous acid are precipitated, to be purified by collection, re-solution in dilute potash, treatment of the solution with animal charcoal, and precipitation of the filtrate with hydrochloric acid. (Kawalier.)

2. *From Thuja occidentalis.* The decoction of the green parts of *Thuja occidentalis* prepared with alcohol of  $40^\circ$  deposits yellow waxy

flakes on cooling. On subsequently distilling the liquid, alcohol and volatile oil pass over, while resin and a turbid watery liquid remain. This liquid contains tannic acid, sugar and pinipicrin, and serves for the preparation of pinipicrin (see below). The resin is dissolved in boiling alcohol of 40°; the still dissolved wax is precipitated by alcoholic acetate of lead; the filtrate treated with sulphuretted hydrogen, which precipitates chlorophyll and sulphide of lead; these substances are removed; and the alcohol is separated from the filtrate by distillation. The remaining liquid deposits a semi-fluid resin, which is to be dissolved in dilute potash-ley, mixed with chloride of calcium, to remove the alpha-thuja resin, filtered from the precipitate, and treated with hydrochloric acid, which precipitates yellowish-white flocks, consisting of a mixture of kinovous acid and beta-thuja resin, to be dissolved, after washing, in lime-water. Carbonic acid passed into this solution throws down a mixture of kinovous acid and carbonate of lime, from which the former may be extracted by ether, and obtained in the solid state by evaporating the ether over the water-bath. — The beta-thuja resin remains dissolved after the carbonic acid has been passed through the liquid, as just mentioned, and may be precipitated from the filtrate by hydrochloric acid.

*Properties.* White or slightly yellow brittle mass, converted by trituration into a strongly electric powder.

<i>In vacuo.</i>				<i>Kawaler.</i>			
				<i>a.</i>	<i>b.</i>		
24 C.....	144	....	70·93	.....	70·55	....	70·82
19 H .....	19	....	9·36	.....	9·48	....	9·40
5 O .....	40	....	19·71	.....	19·97	....	19·78
<hr/>				<hr/>			
C <sup>24</sup> H <sup>19</sup> O <sup>5</sup> .....	203	....	100·00	....	100 00	....	100·00

*a.* from Pine-needles; *b.* from *Thuja*.—So, according to Kawaler. To bring the formula into accordance with the principles of this work, the acid dried in vacuo must be supposed to contain 1 at. H<sub>2</sub>O more. (Kr.)

*Kinovite of Silver.*—Obtained by dissolving the acid in lime-water and precipitating with nitrate of silver.—White, but becomes grey after drying in vacuo. Detonates when heated, but not so strongly as oxalate of silver. Contains 74·11 p. c. oxide of silver, and is therefore C<sup>24</sup>H<sup>19</sup>O<sup>5</sup>, 5 AgO (Kawaler); by calculation, 74·2 p. c. AgO.

#### *Appendix to Kinovous Acid.*

1. *Pinicorretin* C<sup>24</sup>H<sup>19</sup>O<sup>5</sup> (Kawaler, *Wien. Akad. Ber.* 11, 359).—Found in the bark of *Pinus sylvestris*.—The bark of the upper parts of the stem, after being freed from the outer rind, is cut in pieces, and boiled with alcohol of 40°; the ceropic acid which separates from the decoction on cooling is separated by filtration; the greater part of the alcohol evaporated; the residual liquid mixed with water; and the turbid liquid treated with neutral acetate of lead, whereby pinicortannic acid and pinicorretin are precipitated, while cortepinitannic acid and sugar remain in solution. The washed lead-precipitate, digested with very dilute acetic acid, separates into *pinicortannic acid*,

which dissolves (and may be obtained from the solution by precipitating with basic acetate of lead, decomposing the precipitate with sulphuretted hydrogen, and evaporating the filtrate out of contact with the air), and a dark-coloured glutinous residue, which dissolves in strong alcohol. On treating the solution with sulphuretted hydrogen, filtering from the sulphide of lead, and evaporating the filtrate, *pinicorretin* remains behind, and may be purified by dissolving it in alcohol, removing the undissolved portion, and evaporating.

The solution containing cortepinitannic acid and sugar is freed from the former by precipitation with subacetate of lead, which throws down *cortepinitannate of lead*, then filtered, freed from lead by sulphuretted hydrogen, and evaporated over the water-bath; sugar then remains and may be purified from a small quantity of pinipicrin by treatment with anhydrous ether-alcohol.

*Properties.* Black-brown, glutinous mass, almost wholly soluble in ammonia. The ammoniacal solution mixed with chloride of barium yields red-brown flocks of *pinicorretin-baryta*, which may be dried in vacuo.

<i>Pinicorretin-baryta.</i>				Kawalier.	
72 C	432	47.20	47.45		
57 H	57	6.23	6.45		
15 O	120	13.12	13.18		
4 BaO	306	33.45	39.92		
$C^{72}H^{57}O^{15}, 4BaO$				915	107.00

$C^{72}H^{57}O^{15} = 3C^{24}H^{19}O^5$ , therefore isomeric with kinovous acid. (Kawalier.)

2. Kawalier's *Resin from Pinus sylvestris*.—(Kawalier, *Wien. Akad. Ber.* 11, 347.)—In the needles of *Pinus sylvestris* (see page 33). The compound of resin and lime precipitated by chloride of calcium in the preparation of kinovous acid, dissolves almost completely in ether. The ethereal solution is separated from the residue by filtration, and evaporated; the residue is treated with alcohol of  $40^\circ$ , which dissolves the whole, excepting the lime and a small portion of the resin; the solution is again evaporated; and the residue is exhausted with water containing hydrochloric acid, whereupon chloride of calcium passes into solution, while a brownish yellow *resin a* remains behind, which, after washing and drying at  $100^\circ$ , has the consistence of castor oil, and after cooling is brown and of the consistence of salve. If the *resin a* be mixed with a sufficient quantity of hydrate of lime, to make it appear pulverulent, then distilled, and the distillate collected in two portions, two oils are obtained, which, after rectification with water, drying over chloride of calcium and rectifying *per se*, constitute the *oils b* and *c*. These oils twice distilled over anhydrous phosphoric acid, yield the *hydrocarbon d*.

<i>Resin a.</i>		Kaw.	<i>Oil b.</i>		Kaw.	<i>Oil c.</i>		Kaw.
50 C	77.30	77.44	30 C	84.9	84.92	50 C	86.2	85.92
40 H	10.30	10.63	24 H	11.3	11.62	40 H	11.5	11.48
6 O	12.40	11.93	1 O	3.8	3.46	1 O	2.3	2.65
$C^{50}H^{40}O^6$		100.00	$C^{30}H^{24}O$		100.00	$C^{50}H^{40}O$		100.00
<i>Hydrocarbon d.</i>				Kaw.				
20 C				88.24	88.14			
16 H				11.76	11.85			
$C^{20}H^{16}$				100.00	99.99			

*Resin α* is perhaps a mixture of  $C^{40}H^{32}O^5$  and  $\frac{1}{4} C^{40}H^{32}O^4$ ; the *oils b* and *c*, mixtures of oxygenated and non-oxygenated oil, the former of which is decomposed by distillation over phosphoric anhydride. (Kawalier.)

If *resin α* in the fused state be dropped upon soda-lime heated to  $220^\circ$ , a thick colourless oil passes over, which, after dehydration over chloride of calcium, has the composition of *oil e*. The residue dissolves partially when suspended in water; and if the filtrate be precipitated by hydrochloric acid, the precipitate dissolved in potash-ley, the solution treated with animal charcoal, and again precipitated with hydrochloric acid, *resin f* is precipitated as an ash-grey powder, which softens at  $100^\circ$ , and dissolves in alcohol and in alkaline liquids. The undissolved portion decomposed by dilute hydrochloric acid, deposits a resin nearly insoluble in potash, sparingly soluble in alcohol, easily in ether; and the ethereal solution treated with animal charcoal, filtered and evaporated, yields *resin g*, which is light-yellow, brittle, and softens at  $100^\circ$ .

<i>Oil e.</i>		Kaw.	<i>Resin f.</i>		Kaw.	<i>Resin g.</i>		Kaw.
100 C ....	81.1 ....	81.25	50 C ....	72.82 ....	72.62	10 C ....	78.95 ....	79.09
84 H ....	11.4 ....	11.75	40 H ....	9.71 ..	9.82	8 H ....	10.52 ....	10.90
7 O ....	7.5 ....	7.00	9 O ....	17.47 ....	17.56	O ....	10.53 ....	10.01

---

$C^{100}H^{84}O^7$	100.0 ....	100.00	$C^{50}H^{40}O^9$	100.00 ....	100.00	$C^{10}H^8O$	100.00 ....	100.00
--------------------	------------	--------	-------------------	-------------	--------	--------------	-------------	--------

Hence the original resin splits up into products comparatively rich and comparatively poor in oxygen. *Oil e* is perhaps a mixture of  $C^{20}H^{16}$  and  $C^{20}H^{16}, 2HO$ . (Kawalier.)

3. *Beta-thuja resin*,  $C^{40}H^{22}O^{11}$ . (Kawalier, *Wien. Akad. Ber.* 13.524.) The two resins found by Kawalier in the green parts of *Thuja occidentalis* are here distinguished as Alpha- and Beta-thuja resin. — Obtained in the preparation of kinovous acid as described at page 33, and purified by solution in ether. Transparent resin, yielding a lemon-yellow powder.

			Kawalier.
40 C .....	240 ....	68.37 .....	68.39
23 H .....	23 ....	6.55 .....	6.78
11 O .....	88 ....	25.08 .....	24.83

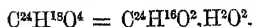
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$C^{40}H^{22}O^{11}$	.....	351 ....	100.00 .....	100.00
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The precipitate which is thrown down by chloride of calcium in the preparation of kinovous acid, and contains the alpha resin, dissolves for the most part in ether, and remains behind when the ether is evaporated; it is still however a mixture of lime and several resins, which are but partially separated even by alcohol. (Kawalier.)

*Oxygen-nucleus*  $C^{24}H^{16}O^2$ .

### Thymoïlol.



LALLEMAND. *N. Ann. Chim. Phys.* 49, 164.

The final product of the action of reducing agents on thymoïl, (p. 36).



Colourless, four-sided, tasteless prisms which melt at  $145^\circ$  and distil without decomposition at  $290^\circ$ .

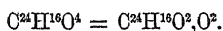
<i>In vacuo.</i>				Lallemand.	
24 C .....	144	....	74.23	.....	73.91
18 H .....	18	....	9.28	.....	9.18
4 O .....	32	....	16.49	.....	16.91
<hr/>					
$C^{24}H^{18}O^4$ .....	194	....	100.00	.....	100.00

Homologous with hydrokinone (xi, 161), and related to thymoïl in the same manner as hydrokinone to kinone.

Converted by *oxydising agents*, e.g., by nitric acid, chlorine-water, nitrate of silver, and bichromate of potash, first into thymeïd, then into thymoïl,

Dissolves sparingly in *water*, very easily in *alcohol* and in *ether*.

### Thymoïl.



A. LALLEMAND. *Compt. rend.* 38, 1022; *J. pr. Chem.* 62, 295; *Pharm. Centr.* 1854, 513; Report by Dumas & Bussy, *Compt. rend.* 39, 723; *Compt. rend.* 43, 375; Fully and with corrections: *N. Ann. Chim. Phys.* 49, 163; abstr. *Ann. Pharm.* 102, 119.

*Formation.* By the action of peroxide of manganese or chromate of potash and sulphuric acid on sulphothymic acid (xiii., 419).

*Preparation.* Thymol is dissolved in excess of oil of vitriol; the resulting sulphothymic acid is diluted with 5 or 6 times its bulk of water, and this liquid is distilled with peroxide of manganese. Water then passes over, together with formic acid, and an orange-coloured oil which soon solidifies, while in the retort there remains a solid brown acid which dissolves in alcohol. The solidified distillate is purified by washing with water, and crystallised from ether-alcohol.

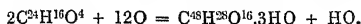
*Properties.* Four-sided laminae, having a fine orange-yellow colour and strong lustre, melting at  $48^\circ$  to a dark-coloured liquid, giving off copious vapours at  $100^\circ$ , and boiling with partial decomposition at  $230^\circ$ . Heavier than water. Has an aromatic odour like iodine and chamomile.

				Lallemand.	
				<i>mean.</i>	
24 C .....	144	....	75.00	.....	75.06
16 H .....	16	....	8.33	.....	8.07
4 O .....	32	....	16.67	.....	16.87
<hr/>					
$C^{24}H^{16}O^4$ .....	192	....	100.00	.....	100.00

Homologous with kinone (xi, 158).

*Decompositions.* 1. Thymoïl blackens quickly when exposed to *light*, and is converted into a mixture of oxythymoïl, thymoïlol, and thymeïd.

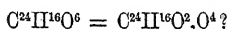
—2. It is partially decomposed by *distillation*, leaving a brown-red residue, which solidifies to a bronze-coloured mass having a metallic lustre. The distillate contains a little oxythymoïl.—3. Thymoïl mixed with aqueous potash rapidly absorbs *oxygen* from the air, and is converted into thymoïlate of potash. 1 at. thymoïl takes 6 at. oxygen.



4. By *hydrogen* in the nascent state, by *sulphurous acid*, *ferrous sulphate*, or *stannous chloride*, thymoïl is converted, first into thymeïd, then into thymoïlol. A similar action may likewise be exerted by the aqueous formic acid produced in the preparation of thymoïl.—5. *Chlorine*, with aid of heat, slowly decomposes thymoïl, forming chlorinated products.—6. Thymoïl absorbs *ammonia gas*, and is converted into thymoïlamide.

Thymoïl dissolves in warm *oil of vitriol* and in warm concentrated *nitric acid*, and is precipitated in its original state by water.—It dissolves sparingly in *alcohol*, very easily in *ether*.

### Oxythymoïl.



LALLEMAND. *N. Ann. Chim. Phys.* 49, 167 (see page 36).

1. Thymoïl enclosed in a sealed tube, is exposed for some days to the sun's rays, and the resulting black mass is washed with alcohol, which dissolves thymoïlol and thymeïd, and leaves a small quantity of oxythymoïl undissolved.—2. In the dry distillation of thymoïl, a small quantity of oxythymoïl is formed, and may be obtained in the separate state by dissolving out the other products with alcohol.

*Properties.* Crystalline powder of a fine lemon-yellow colour, melting at 190°.

Lallemand.					
24 C .....	144	....	69·23	.....	69·25
16 H .....	16	....	7·69	.....	7·61
6 O .....	48	....	23·08	.....	23·14
<hr/>					
C <sup>24</sup> H <sup>16</sup> O <sup>6</sup> .....	208	....	100·00	.....	100·00

Insoluble in *water* and in aqueous alkalis, and not altered by the greater number of reagents.

Insoluble in *alcohol*, very slightly soluble in *ether*.

### Appendix to Oxythymoïl.

### Thymoïlic Acid.

LALLEMAND. *N. Ann. Chim. Phys.* 49, 166.

Compare page 36.

When crystals of thymoïl are shaken up with potash-ley in contact with the air, they dissolve with red-brown colour, forming thymoïlate

of potash, which may be obtained pure by saturating the liquid with carbonic acid, evaporating, and exhausting the residue with absolute alcohol. — Hydrochloric acid added to the solution of thymoilate of potash throws down thymoic acid in dirty yellow flocks, very slightly soluble in water.

The *thymoïlates* are soluble in water, excepting the *lead* and *silver salts*. The former contains 43.02 p. c. oxide of lead, and is therefore  $C^{48}H^{28}O^{16}$ ,  $3PbO$  (calc. 43.07 PbO). (Lallemand.)

*Conjugated Compound.*

**Thymeïd.**



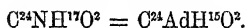
LALLEMAND. *N. Ann. Chim. Phys.* 49, 165.

*Formation and Preparation.* 1. By bringing thymoïl in contact with thymoïlol. If the two bodies, dissolved in boiling alcohol or ether, be mixed in equal quantities, the mixture instantly assumes a blood-red colour, and yields crystals of thymeïd by cooling or evaporation. — 2. Thymeïd is the first product formed by the action of reducing agents on thymoïl. It is produced for example by sulphurous acid, when crystals of thymoïl are thrown into it, and more slowly by ferrous sulphate and stannous chloride. — 3. Thymeïd is also the first product of the action of oxydising agents on thymoïlol (p. 57).

*Properties.* Crystals of a fine violet colour, exhibiting by reflected light a bronze-coloured metallic reflection, like the wings of beetles.

*Oxyamidogen-nucleus*  $C^{24}AdH^{15}O^2$ .

**Thymoïlamide.**



LALLEMAND. *N. Ann. Chim. Phys.* 49, 166.

Thymoïl in the fused state slowly absorbs ammonia-gas, and is converted into a dark red amorphous mass, which is hard and brittle at common temperatures, but softens at  $100^\circ$ , and may then be drawn into threads. It is soluble in alcohol.

*Primary Nucleus*  $C^{24}H^{20}$ ; *Oxygen-nucleus*  $C^{24}H^{14}O^6$ ?

**Globularetin.**

G. F. WALZ. *N. Jahrb. Pharm.* 13, 281.

Produced, together with paraglobularetin and sugar, when globularin is boiled with acids.

The resin obtained by boiling globularin with dilute sulphuric acid is washed with water and dissolved in alcohol; the alcoholic solution is diluted and the residue treated with ether, which dissolves the globularetin, leaving paraglobularetin undissolved.

White powder, melting at the heat of the hand.

					Walz. mean.
24 C .....	144	...	69.90	.....	70.04
14 H .....	14	...	6.79	.....	6.88
6 O .....	48	...	23.31	.....	23.08
<hr/>					
$C^{24}H^{14}O^6$ .....	206	...	100.00	.....	100.00

### Paraglobularetin.



G. F. WALZ. *N. Jahrb. Pharm.* 13, 281.

Produced, together with globularetin, by boiling globularin with acids, and may be obtained by solution in alcohol and precipitation by water, as a coloured powder, insoluble in ether.

<i>Dried.</i>					Walz.
24 C .....	144	...	64.28	...	62.95
16 H .....	16	...	7.14	...	7.17
8 O .....	64	...	28.58	...	29.88
<hr/>					
$C^{24}H^{16}O^8$ .....	224	...	100.00	...	100.00

Walz erroneously calculates the mean of his analyses at 64.3 p. c. carbon. (Kr.)

### Primary Nucleus $C^{24}H^{22}$

### Naphthol.



Occurs, according to Pelletier & Walter, in the naphtha of Amiano (xii. 439), and is obtained by fractionally distilling rock-oil, which has previously been repeatedly treated with cold oil of vitriol, and collecting the portion which passes over at 190°. Vapour-density = 5.3. The distillate obtained at 115° consists chiefly of naphthene  $C^{16}H^{16}$ , which has a vapour-density of 4.0, and contains 84.6 p. c. C and 14.7 H. (*J. Pharm.* 26, 565.)

Pelletier & Walter.					Vol.	Density.
24 C .....	144	...	86.74	...	C-vapour	24
22 H .....	22	...	13.26	...	H-gas	22
<hr/>						
$C^{24}H^{22}$ ....	166	...	100.00	...	Naphthol-vapour	2
						1
						11.5086
						5.7543

The sample analysed probably contained naphthene as well as naphthol. (Pelletier & Walter).

*Oxygen-nucleus*  $C^{24}H^{20}O^2$ .

### Wormseed Oil.



This oil belongs to the 24-carbon group, and should therefore have been treated in this place, instead of in vol. xiv. p. 316. Vapour-density 6.4 ( $C^{24}H^{20}O^2 = 6.24$ ). Sp. gr. of the oil at  $13^\circ = 0.9201$ . (Kraut.)

### Onocerin.



HLASIWETZ. *Wien. Akad. Ber.* 15, 162.

*Occurrence.* In the root of *Ononis spinosa*.

*Preparation.* The root is boiled with alcohol; the dark brown tincture freed from alcohol by distillation; the residue evaporated to a syrup, and the crystals which separate after some days are collected, and purified by pressing, washing with cold alcohol, and recrystallisation from boiling alcohol, with help of animal charcoal.

*Properties.* Small, hard, very light, capillary crystals, having a fine satiny lustre. Tasteless and inodorous. Becomes strongly electric by friction. Melts when heated, and solidifies in the crystalline form. Neutral.

	at $100^\circ$ .			Hlasiwetz. mean.	
24 C.....	144	....	80.00	.....	79.84
20 H.....	20	....	11.11	.....	11.31
2 O.....	16	....	8.89	.....	8.85
<hr/>					
$C^{24}H^{20}O^2$ .....	180	....	100.00	.....	100.00

$C^{12}H^{10}O$ , according to Hlasiwetz, but doubled here according to the system of the Handbook.

*Decomposition.* Gives off an odour like that of incense when heated; burns with flame and leaves an easily combustible charcoal. — It is scarcely altered by *chlorine* at mean temperatures, but at higher temperatures it is converted, with evolution of hydrochloric acid, into chloronocerin.

Onocerin is insoluble in *water*; scarcely altered by *ammonia*, *hydrochloric acid*, or *potash-ley*. Its alcoholic solution neither reduces *nitrate of silver*, nor precipitates other *metallic salts*.

It dissolves in *oil of vitriol*, forming a yellowish solution, which is not altered by *peroxide of manganese*.

It dissolves in boiling *alcohol*, and is abundantly precipitated by *water*.

It dissolves but sparingly in *ether*, easily in warm *oil of turpentine*.

Oxygen-nucleus  $C^{24}H^{14}O^8$ .

### Parsley-camphor.

$C^{24}H^{14}O^8$ .

DEHNE (1778). *Crell. Chem. J.* 1, 40.

BOLLE. *Br. Arch.* 29, 168.

BLEY. *N. Tr.* 14, 2, 134; *N. Br. Arch.* 63, 267.

BLANCHET & SELL. *Ann. Pharm.* 6, 301; abstr. *N. Br. Arch.* 24, 208; *Repert.* 70, 163.

RUMP. *Repert.* 56, 21.

LÖWIG & WEIDEMANN. *Pogg.* 46, 55; abstr. *N. Br. Arch.* 24, 208; *Repert.* 70, 163.

LOOSE. *N. Br. Arch.* 63, 287.

#### *Stearoptene of Oil of Parsley, Petersilien-campher.*

*Occurrence.* In the herb and seed of parsley (*Apium Petroselinum* L.), together with volatile oil.—May be extracted from the seed by alcohol. (Rump.)

*Preparation.* The seed (Pabitzky, *Braunsch. Anz.* 1754, 1205), or the fresh herb (Dehne), is distilled with water, and the crystals which separate from the distillate are collected (Bley, Martius, *Repert.* 39, 246), pressed between blotting paper (Bolle, Rump), and recrystallised from alcohol (Blanchet & Sell).—The heavier oil which passes over towards the end solidifies after half a year's standing. (Dehne.)—The camphor is chiefly contained in the oil which distils over with the water; but the oil which goes over in the early part of the distillation, likewise solidifies partially. (Rump.)—When oil of parsley is fractionally distilled till the residue solidifies, that residue does not contain any parsley-camphor, but consists merely of resin. (Löwig & Weidmann.)—The watery distillate of parsley-seed deposits, in addition to the camphor, a yellow powder, formed from the camphor by oxidation. (Loose.)

Parsley seed yields 12.5 per cent. (?) of parsley-camphor (Pabitsky); 0.21 per cent. (Rump).

*Properties.* White, slender, six-sided needles. (Blanchet & Sell.) Prisms 2—6 inches long, with their terminal faces truncated (Bley), and having a silky lustre. (Rump.)—Heavier than water. (Bolle.)—Melting point 30°. (Blanchet & Sell; Rump.)—Boils, with decomposition at about 300°. (Blanchet & Sell.)—Not sublimable (Blanchet & Sell); partially (Bley).—Solidifies at 21° (Blanchet & Sell); at 18°, however, if it has been previously heated to the boiling point (Blanchet & Sell); at 6.3°, forming a white, pearly mass. (Loose.) Makes spots on paper, which are difficult to remove. (Loose.) Has a faint odour of parsley, and a burning camphorous taste, with irritating after-taste. Neutral.

				Blanchet & Sell.	
				mean.	
24 C.....	144	....	64.86	.....	64.62
14 H.....	14	....	6.30	.....	6.39
8 O.....	64	....	28.84	.....	28.99
$C^{24}H^{14}O^8$ .....	222	....	100.00	.....	100.00

*Decompositions.* 1. When *heated*, it melts, turns brown, gives off irritating vapours, and volatilises, depositing on the glass tube drops of liquid, which solidify in the crystalline form. (Bley, *vid. sup.*)—2. When *set on fire*, it burns with a slightly smoky, feebly luminous flame. (Loose.)—3. Detonates sharply with *bromine*.—4. Triturated with *iodine* and then warmed, it yields a brown viscid mass soluble in alcohol. (Bolle.)—5. With strong *nitric acid*, it becomes heated, gives off nitrous acid and forms a yellowish solution (Bolle), containing oxalic acid (Rump); not containing oxalic acid. (Martius.) The solution mixed with water deposits a yellow resinous powder. (Bolle.) The solution of the camphor in fuming nitric acid, the formation of which is attended with effervescence, is not precipitated by water or aqueous ammonia. (Bley.)—6. Parsley-camphor is not altered by cold *oil of vitriol*, but hot oil of vitriol colours it dark red, and at higher temperatures brown. (Bley.)

*Combinations.* With *Oxygen?*—Parsley-camphor appears to be converted, by absorption of oxygen, into a yellow body, which is deposited, together with the camphor itself, in old parsley-water. (Loose.)—This yellow body is pulverulent, and nearly tasteless, but leaves a slightly bitter after-taste. When heated, it melts, gives off choking vapours, loses its yellow colour, which, however, may be restored by rubbing, breathing upon, or moistening the solidified mass; at a stronger heat, it sublimes, and, when set on fire, burns with flame, leaving a residue of charcoal. Strong nitric acid colours it yellow and then dissolves it, with evolution of nitrous acid; fuming nitric acid chars it. It dissolves in acetic acid, also in cold alcohol, and more freely in warm alcohol, but less so than parsley-camphor; the solution is rendered turbid by water. The yellow substance dissolves in ether. (Loose.)

Parsley-camphor dissolves slightly in cold *water* (Bolle, Rump); more easily in hot water, slightly in *hydrochloric acid*, *aqueous potash* and *ammonia*. (Bley.) It is not soluble in aqueous potash. (Bolle, Loose.)

It dissolves readily in *absolute alcohol*, less in alcohol of sp. gr. 0.87. (Bolle.) This solution yields a crystalline precipitate with water (Bley), and a yellow powder by spontaneous evaporation.

It dissolves in *ether*, and in *oils*, both *fixed* and *volatile*. (Bolle, Loose.)

*Oxychlorine-nucleus*  $C^{24}Cl^2H^{18}O_2$ .

### Chloronocerin.

$C^{24}Cl^2H^{18}O_2$ .

HLASIWETZ. *Wien. Akad. Ber.* 15, 163.

Chlorine gas is passed over onocerin heated by the water-bath, and the mass, which becomes somewhat brown, fusible and amorphous, is pulverised, and again exposed to the action of the chlorine, which is ultimately supported by heating the resin in a salt-bath, as long as hydrochloric acid continues to form. The resulting resinous mass is

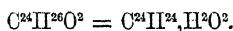
purified by repeated solution in ether, till it is left by the evaporation of the ether in the form of a white powder.

Chloronocerin melts on platinum, and burns with an odour of resin and hydrochloric acid. — In warm *nitric acid*, it melts and oxidises. — It is turned brownish by *oil of vitriol*, and afterwards not further altered by *peroxide of manganese*. It is insoluble in *water*, *ammonia*, *potash-ley* or *alcohol*; very easily in *ether*.

	at 100°.		Hlasiwetz.	
24 C .....	144	....	57·8	..... 57·4
2 Cl.....	71	....	28·4	..... 27·5
18 H .....	18	....	7·2	..... 7·1
2 O .....	16	....	6·6	..... 8·0
<hr/>				
C <sup>24</sup> Cl <sup>2</sup> H <sup>18</sup> O <sup>2</sup> .....	249	....	100·0	..... 100·0

*Primary Nucleus* C<sup>24</sup>H<sup>24</sup>.

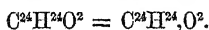
**Lethal.**



HEINTZ. *Pogg.* 93, 519; abstr. *Ann. Pharm.* 92, 299; *Berl. Akad. Ber.* 1854, 562; *J. pr. Chem.* 63, 364; *Pharm. Centr.* 1854, 907. — *J. pr. Chem.* 66, 19.

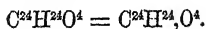
Not obtained in the pure state. — In the saponification of commercial spermaceti, salts of stearic, palmitic, myristic, and lauric acids are obtained, together with crude ethal. When the latter is recrystallised from alcohol, pure ethal C<sup>32</sup>H<sup>34</sup>O<sup>2</sup> crystallises out, whilst the homologous compounds, stethal C<sup>36</sup>H<sup>38</sup>O<sup>2</sup>, methal C<sup>28</sup>H<sup>30</sup>O<sup>2</sup>, and lethal C<sup>24</sup>H<sup>26</sup>O<sup>2</sup>, remain, in smaller quantity, in the mother-liquors, inasmuch as the alcohols obtained from these mother-liquors (after removal of the admixed fatty acids by repeated treatment with alcoholic potash and addition of water) yield, when heated to 275°–280° with potash-lime as long as hydrogen continues to escape, stearic, palmitic, myristic and lauric acids. (Heintz.) Compare also Scharling (*Ann. Pharm.* 96, 236) & Heintz's reply (*Ann. Pharm.* 97, 271).

**Lauric Aldehyde.**



Exists, according to Gr. Williams, in the portion of volatile oil of rue which distils at 232° (see xiv. 489.).

**Lauric Acid.**



MARSSON (1842). *Ann. Pharm.* 41, 33.

STEAMER. *Ann. Pharm.* 53, 393.



GÖRGEY. *Ann. Pharm.* 66, 303; *Pharm Centr.* 1849, 8; *N. Ann. Chim. Phys.* 25, 102.

HEINTZ. *Pogg.* 92, 429 & 583; *Berl. Akad. Ber.* 1854, 207; *Ann. Pharm.* 92, 291; *J. pr. Chem.* 62, 349 & 482; 63, 162; *N. Phil. Mag. J.* 9, 74; *N. J. Pharm.* 26, 313. — *Pogg.* 93, 519; *Berl. Akad. Ber.* 1854, 562; *J. pr. Chem.* 63, 364; *Lieb. Kopp. Jahresber.* 1854, 456 & 460. — Collection of HEINTZ's Researches on the Fats: *J. pr. Chem.* 66, 1.

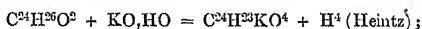
A. C. OUDEMANS, JUN. *J. pr. Chem.* 81, 356 & 357.

*Laurostearic acid* (Marsson). *Pichurimtalgsäure* (Sthamer). *Pekurimsäure*.

*Sources.* In the fat of the bay-tree (Marsson); in the fat of pichurim beans (Sthamer); also in the volatile oil of these beans. (Al. Müller, *J. pr. Chem.* 58, 469.) In small quantity, together with many other acids, in spermaceti (Heintz), in croton oil (Schlippe, *Ann. Pharm.* 105, 14), in the fruit of *Cylicodaphne sebifera*. (Gorkom, *Tydschrift f. Neerl. Indie.* 81, 410.) — In the fruit of *Mangifera Gabonensis*, the so-called Dika bread, together with myristic acid, but unaccompanied by any other acids. (Oudemans.) In the *Age* or *Axin* of the Mexicans, a salve-like fat obtained from *Coccus Axin*. (Hcppe, *J. pr. Chem.* 80, 102.)

In cocoa-nut oil. (Görgey, Oudemans.) This oil contains, according to Brandes (*N. Br. Arch.* 65, 115), a solid fatty acid, melting between  $25^{\circ}$  and  $27^{\circ}$  = cocinic acid, or, according to Pelouze & Boudet, elaidic acid. Bromeis (*Ann. Pharm.* 35, 277) designated the acid melting at  $35^{\circ}$ , obtained by repeatedly crystallising the fatty acids of cocoa-nut oil, as *cocostearic acid*, and assigned to it the formula  $C^{27}H^{27}O^4$ , which Heintz (who thought that he had previously [*Pogg.* 87, 21, and 267] found this acid in spermaceti), by calculating from the new atomic weight of carbon, altered to  $C^{26}H^{26}O^4$ . The latter acid Heintz designates as *cocinic acid*. St. Evre's cocinic acid (*N. Ann. Chim. Phys.* 20, 91), likewise from cocoa-nut oil, is prepared as follows:—The oil is saponified; the acids separated, pressed, crystallised from alcohol, dissolved in soda-ley, and precipitated with acetate of lead; the precipitate exhausted with ether; and the residue decomposed by tartaric acid. According to St. Evre, it is composed of  $C^{26}H^{26}O^4$ , and melts at  $34.7^{\circ}$ . But according to the investigations of Görgey and Oudemans, which agree with each other, cocoa-nut oil does not contain any acid possessing the properties assigned by Brandes, Bromeis, or St. Evre to cocinic acid; the oil appears rather to contain small quantities of palmitic and myristic acids, together with large quantities of lauric, capric, caprylic, and caproic acids, the last two having been previously found in it by Fehling. Respecting the former results, see Oudemans (*J. pr. Chem.* 81, 367.)

*Formation.* By heating ethal with potash-lime to  $275^{\circ}$  —  $280^{\circ}$ , (Heintz, Scharling.) According to Heintz, it is produced only from mixed (crude) ethal, inasmuch as this substance contains lethal (p. 43).



but, according to Scharling, it is obtained from the ethal itself  $C^{32}H^{34}O^2$ , which, according to him, is decomposed by heating with potash-lime, in such a manner as to yield stearic, palmitic, myristic, lauric and butyric acids. (Scharling, *Ann. Pharm.* 96, 236; Heintz, *Ann. Pharm.* 97, 271.)

*Preparation.* 1. *From Bay-fat.* Laurostearin from *Ol. laurin unguinos*. Is saponified with potash-ley, the soap is separated by common salt, and its hot aqueous solution is decomposed with tartaric acid. The lauric acid then rises to the surface in the form of an oil which solidifies on cooling; and is freed from adhering tartaric acid by repeated fusion with water. (Marsson.)

2. *From Piclurim beans.* Laurostearin from *Faba piclurim maj.* is saponified with potash-ley till a clear soap-jelly is formed; common salt is added, and the white, brittle soda-soap thus produced is dissolved in boiling water, and supersaturated at the boiling heat with hydrochloric acid; lauric acid then rises to the surface as a colourless oil, which on cooling solidifies to a white crystalline mass. It is freed from hydrochloric acid by repeated washing with water and purified by repeated crystallisation from weak alcohol. (Sthamer.)

3. *From Cocoa-nut oil.* The oil is saponified with weak potash-ley; the soap decomposed by dilute sulphuric acid, and the mixture distilled as long as fatty acids pass over, the water being repeatedly poured back. The distillate neutralised with potash solidifies on evaporation to a gelatinous soap, which is separated by common salt, repeatedly dissolved in potash, and again separated with salt, to free it from the fatty acids which can be thus removed, and again decomposed with dilute sulphuric acid. It is then neutralised with ammonia; the solution precipitated by chloride of barium; the liquid strained off; and the baryta-salts which remain repeatedly boiled with water. The resulting solutions, as they run from the funnel, immediately deposit loose flocks of laurate of baryta, and the liquid, as it cools down, becomes turbid and deposits pulverulent caprate of baryta. (Görgey; comp. also *Prep.* 5.)

4. *From Spermaceti.* The saponification of this substance yields, besides ethal, considerable quantities of stearic, palmitic, and myristic acids, and smaller quantities of lauric acid. — The solution of 10 lbs. of purified spermaceti in 30 lbs. alcohol is boiled for some time with  $4\frac{1}{2}$  lbs. caustic potash previously dissolved in alcohol; the solution precipitated with aqueous chloride of barium, and strained while hot; the still warm residue pressed as strongly as possible in a warmed press; then well moistened with alcohol and again pressed; the alcohol distilled off from the solutions; the residue freed from the whole of the soluble matter by repeated treatment with ether; and the portion insoluble in ether added to the baryta-salts previously obtained. In this manner are obtained, on the one hand, crude ethal, on the other, the baryta-salts of the fatty acids of spermaceti.

The baryta-salts suspended in water are boiled with very dilute hydrochloric acid, till the supernatant oily layer appears perfectly clear; the fatty acids thus obtained are dissolved in alcohol; the solution is left to cool; and the crystals which separate are pressed, first alone, then several times after being moistened with alcohol, whereby a mixture of palmitic and stearic acids is obtained, while a portion of these two acids and the whole of the myristic and lauric acids remain in solution.

The whole of the mixed alcoholic solutions are heated; a concentrated aqueous solution of acetate of magnesia is added, so as to precipitate about  $\frac{1}{20}$  of the quantity of fatty acids present; the precipitate which forms on cooling is separated by filtration; acetate of magnesia is added to the filtrate in about the same quantity as before; and the same treatment is repeated (the liberated acetic acid being neutralised towards the end with ammonia), till acetate of magnesia no longer forms any precipitate, even in presence of excess of ammonia. In this manner a number of magnesia-salts (19) are obtained, from which stearic, palmitic and myristic acids may be separated, by processes to be hereafter described in connection with these acids.

The alcoholic solution, from which everything precipitable by acetate of magnesia in presence of excess of ammonia has been thus removed, still retains lauric acid together with myristic and oleic acids. It is precipitated with acetate of lead; the precipitate is washed with dilute alcohol, dried, and freed from a small quantity of oleate of lead, by treatment with ether; and the undissolved portion is decomposed by prolonged and repeated boiling with very dilute hydrochloric acid, whereby a mixture of acids melting at  $39.7^{\circ}$  is separated. By repeatedly crystallising this mixture from alcohol, as long as the separated acid exhibits a rise of melting point, lauric acid is ultimately obtained, melting at  $43.6^{\circ}$ , and not capable of further decomposition by partial precipitation with acetate of baryta, while myristic acid remains in solution. (Heintz.)

5. From spermaceti or other fats containing lauric acid, provided they are free from oleic acid, or this acid has been removed by the process to be described below. — The fat is saponified with (alcoholic) potash; the fatty acids are separated from the ethal or the glycerin, as above described, and dissolved in 10 pts. of hot alcohol; the solution is left to cool slowly in a cellar; and the fatty acids which crystallise out are separated by filtration and pressure. The mother-liquor is diluted with an equal quantity of boiling alcohol and supersaturated with ammonia; acetate of magnesia is added in excess to remove a certain portion of the fatty acids; the alcohol distilled off from the filtrate; the remaining salts decomposed by boiling with dilute hydrochloric acid; the separated acids redissolved in a quantity of hot alcohol sufficient to retain them in solution after cooling; and a concentrated solution of acetate of baryta, equal to about  $\frac{1}{2}$  of the weight of the fatty acids, is repeatedly added, as long as a precipitate is thereby formed on cooling. The precipitates last obtained, which contain chiefly lauric acid, are separately decomposed by boiling dilute hydrochloric acid, and each portion of acid thereby liberated, whose melting point lies above  $43.6^{\circ}$ , is separately and repeatedly crystallised from diluted alcohol till its melting point has risen to  $43.6^{\circ}$ . (Heintz.)

If the fat contains oleic acid, it is saponified, the fatty acid is separated and mixed with a small quantity of hot alcohol, and the solid portions are removed by submitting the cooled mass to pressure. The mother-liquor (together with the alcohol used for washing the separated acids) is precipitated with ammonia and neutral acetate of lead; the washed and dried lead-salts are completely freed from oleate of lead by means of ether; the undissolved portion is decomposed by boiling hydrochloric acid; and the separated fatty acids are treated as above. (Heintz.) In this manner pure lauric acid is easily obtained from cocoa-nut oil (which, according to Oudemans, does not contain oleic acid). If the acids dissolved in alcohol be precipitated in small portions with acetate of baryta, the first portions contain palmitic and myristic acids, and from the remaining liquid, lauric acid may be obtained by repeated fractional precipitation or by crystallisation in the cold. (Oudemans.)

*Properties.* Lauric acid solidifies after fusion to a scaly crystalline mass, exhibiting a laminated texture on the fractured surface. (Heintz.) Brittle. (Sthamer.) Crystallises from alcohol (only from weak alcohol according to Sthamer, from strong alcohol not till cooled to  $0^{\circ}$ : Görgzey, Heintz); in white, silky needles, united in tufts

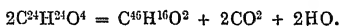
(Sthamer); in prickly glandular masses of the size of hazel-nuts (Görgey); in nearly translucent scales (Heintz). It melts to a colourless oil at 43·6° (Heintz), 42°–43° (Marsson, Görgey), 43° (Sthamer), 45° (Müller), 43·8° (Schlippe), 43·5° (Oudemans).—The alcoholic solution has a slight acid reaction. Sp. gr. 0·883 at 20°. (Görgey.) When boiled with water, it volatilises with the vapour. (Görgey, Oudemans.)

Marsson. Sthamer. Görgey. Heintz.								Oudemans.	
								mean.	at 120°
								a.	b.
24 C	.....144	.... 72·00	.... 72·09	.... 72·06	.... 71·88	.... 71·92	.... 72·01	.... 72·00	
24 H	..... 24	.... 12·00	.... 12·04	.... 11·93	.... 11·95	.... 12·08	.... 12·18	.... 12·17	
4 O	..... 32	.... 16·00	.... 15·87	.... 16·01	.... 16·17	.... 16·00	.... 15·81	.... 15·83	
C <sup>24</sup> H <sup>24</sup> O <sup>4</sup>	.....200	.... 100·00	.... 100·00	.... 100·00	.... 100·00	.... 100·00	.... 100·00	.... 100·00	

Marsson analysed lauric acid from the fat of the bay-tree; Sthamer, that from pichurim beans; Görgey, that from cocoa-nut oil; Heintz, that from spermaceti; Oudemans, *a.* that from Dika bread; *b.* that from cocoa-nut oil. On the formula, see also Pohl (*Wien. Akad. Ber.* 10, 485.)

Isomeric with hordeic acid.

By the distillation of its lime-salt, lauric acid is resolved into laurostearone and carbonate of lime. (Overbeck.)



Lauric acid is perfectly insoluble in *water*. (Heintz.)

*Laurate of Soda*.—Lauric acid is added to a boiling concentrated solution of carbonate of soda, perfectly free from sulphate and chloride, in quantity not quite sufficient for complete saturation; the liquid is evaporated over the water-bath; the soap which remains is dissolved in absolute alcohol, and the filtrate is evaporated to dusty dryness. (Marsson, Sthamer.)—White powder, whose alcoholic solution solidifies on cooling to a white opaque jelly. (Sthamer.) The alcoholic solution becomes turbid when largely diluted with water. (Marsson.)

				Marsson.	A. Müller.
				at 100°.	at 100°.
NaO	..... 31	.... 13·96	.... 13·86	.... 13·86	.... 13·69
C <sup>24</sup> H <sup>23</sup> O <sup>3</sup>	..... 191	.... 86·04			
C <sup>24</sup> NaH <sup>23</sup> O <sup>4</sup>	..... 222	.... 100·00			

*Laurate of Baryta*.—*Preparation* (p. 45). Fine, light, white nacreous powder, consisting of microscopic laminae. (Heintz.)—Light, thin nacreous laminae, presenting under the microscope the appearance of tables made up of slender crystalline needles, somewhat curved. (A. Müller.) Crystallises on cooling from a boiling saturated aqueous solution in snow-white flakes. The saturated alcoholic solution becomes filled, on cooling, with delicate crystalline spangles, which, after drying at 100°, resemble caprate of baryta. (Görgey.) It is wetted by alcohol and ether, but not by water. (Görgey.)—Dissolves in 10,864 pts. of water at 17·5°, in 1982 pts. boiling water, in 1468 pts. cold and 211 pts. hot alcohol. (Görgey.) Decomposes before melting. (Heintz.)

					Görgey.	Heintz.	F. Hoppe.
24 C .....	144	...	53·81	...	53·93	...	54·48
23 H .....	23	...	8·60	...	8·67	...	8·61
3 O .....	24	...	8·97	...	8·95	...	9·25
BaO .....	76·6	...	28·62	...	28·45	...	27·66
$C^{24}H^{23}BaO^4$ .....	267·6	...	100·00	...	100·00	...	100·00

Contains 28·82 per cent. baryta (Al. Müller).

*Laurate of Lime.* — White precipitate, obtained by mixing the solutions of laurate of soda and chloride of calcium.

*Laurate of Lead.* — Snow-white, loose, amorphous powder. (Heintz.) Laminae, having a beautiful nacreous lustre. (Müller.) Melts between  $110^\circ$  and  $120^\circ$ , and solidifies to a dull, amorphous mass. (Heintz.) Melts below  $100^\circ$  to a colourless liquid, which solidifies in the crystalline form on cooling. (Müller.) Insoluble in water. Insoluble in cold, sparingly soluble in boiling, alcohol. (Müller.)

					Heintz.	Müller.
24 C .....	144	...	47·59	...	47·03	
23 H .....	23	...	7·60	...	7·59	
Pb .....	103·8	...	34·24	...	34·49	34·22
4 O .....	32	...	10·57	...	10·89	
$C^{24}H^{23}PbO^4$ .....	302·8	...	100·00	...	100·00	

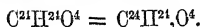
*Laurate of Copper.* — Obtained by precipitating the hot alcoholic solution of the soda-salt with aqueous sulphate of copper. (Oudemans.)

					Oudemans.
24 C .....	144	...	62·34	...	62·34
23 H .....	23	...	9·95	...	10·03
CuO .....	40	...	17·31	...	17·24
3 O .....	24	...	10·40	...	10·39
$C^{24}H^{23}CuO^4$ .....	231	...	100·00	...	100·00

*Laurate of Silver.* — The solution of the soda-salt in weak alcohol is precipitated with nitrate of silver, and the bulky precipitate is collected, washed, and dried. (Marsson, Sthamer.) White powder, consisting of slender microscopic needles. (Heintz.) Dissolves easily in ammonia, and crystallises from the hot concentrated solution in very small needles. (Marsson.) Not altered by light (Marsson), scarcely (Sthamer, Heintz.) Decomposes before fusion. (Heintz.)

					Marsson. at $100^\circ$ .	Sthamer. at $100^\circ$ .	Heintz.	Oudemans.
24 C .....	144	...	46·91	...	47·34	...	46·69	47·60
23 H .....	23	...	7·49	...	7·58	...	7·48	7·84
Ag .....	108	...	35·18	...	34·68	...	35·16	34·82
4 O .....	32	...	10·42	...	10·40	...	10·35	9·74
$C^{24}H^{23}AgO^4$ .....	307	...	100·00	...	100·00	...	100·00	100·00

Lauric acid dissolves very easily in strong alcohol and ether. (Marsson & Sthamer.)

**Hordeic Acid.**

FR. BECKMANN. *J. pr. Chem.* 66, 52; abstr. *N. Ann. Chim. Phys.* 46, 226.

When dried barley is heated with oil of vitriol and water, as in Emmet's method of preparing formic acid (vii. 273), hordeic acid passes over together with aqueous formic acid and furfural, and separates from the distillate in white laminae. These are collected, washed, repeatedly crystallised from alcohol, and freed from water by fusion in an air-bath.

*Properties.* White crystalline laminae, melting at 60° to a colourless oil, which solidifies at 55°. Permanent in the air. Makes grease spots on paper. Acid.

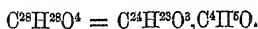
Beckmann.					
24 C.....	144	...	72.00	.....	71.31
24 H.....	24	...	12.00	.....	12.68
4 O.....	32	...	16.00	.....	16.01
<hr/>					
$\text{C}^{24}\text{H}^{24}\text{O}^4$ .....	200	...	100.00	.....	100.00

So, according to Beckmann. Wurtz (*N. Ann. Chim. Phys.* 46, 226), rightly regards the separate identity and the formula of this acid as doubtful.—Isomeric with lauric acid.

*Decompositions.* Burns, without residue, when heated on platinum foil. — Not altered by cold oil of vitriol, but carbonised by that liquid when hot. Decomposed by hot, but not by cold nitric acid.

*Combinations.* Insoluble in water. In contact with alkalis or their carbonates, it forms salts which dissolve in water and alcohol, forming solutions which froth like soap and are precipitated by common salt.

*Hordeate of Silver.* Obtained from the ammonia-salt by precipitation with nitrate of silver. Contains 34.79 p. c. silver. (calc.  $\text{C}^{24}\text{AgH}^{23}\text{O}^4 = 35.18$  p. c. Ag.)

*Conjugated Compounds of Lauric Acid.***Laurate of Ethyl.**

A. GÖRGEY. *Ann. Pharm.* 66, 306; *Pharm. Centr.* 1849, 8; *N. Ann. Chim. Phys.* 25, 102; *Lieb. Kopp. Jahresb.* 1847—1848, 560.  
 DELFFS. *N. Jahrb. Pharm.* 1, 25; *Ann. Pharm.* 92, 277; *Pharm. Centr.* 1854, 276; *Lieb. Kopp. Jahresb.* 1854, 26 and 458.

*Pichurate of Ethyl, Lauric or Pichuric ether, Pichurintalgsaures Äthyl oxyd, Laurinvinester.*

Separates partially when hydrochloric acid gas is passed into alcoholic lauric acid, completely on subsequent addition of water, in the form of an oil, which is washed with water containing soda, then with pure water, dried over chloride of calcium, and rectified.

Transparent, colourless oil, which becomes viscid in the cold, and solidifies to a compact mass at  $-10^{\circ}$ . Sp. gr. 0.86 at  $20^{\circ}$ . (Görgey.) 0.8671 at  $19^{\circ}$ . (Delffs.) Boils at  $269^{\circ}$ , when the barometer stands at 0.75 met. (Delffs.), at  $264^{\circ}$ , with partial decomposition (Görgey). Has an agreeable fruity odour, and a sweetish mawkish taste. Vapour density = 8.4. (Görgey.)

				Görgey.	Delffs.
28 C .....	168	...	73.68	73.41	73.10
28 H .....	28	...	12.28	12.42	12.45
4 O .....	32	...	14.04	14.17	14.45
<hr/>					
$C^{24}H^{20}O^3, C^4H^5O$ .....	228	...	100.00	100.00	100.00
<hr/>					
	Volume.			Density.	
C-vapour .....	28	.....		11.6480	
H-gas .....	28	.....		1.9404	
O-gas .....	2	.....		2.2186	
<hr/>					
Vapour of Laurate of Ethyl	2	.....		15.8070	
				7.9035	

Lauric ether is insoluble in *water*, sparingly soluble in *alcohol*, but dissolves in all proportions in *ether*. (Delffs.)

### Laurostearin.



MARSSON. *Ann. Pharm.* 41, 330.

STHAMER. *Ann. Pharm.* 53, 390.

BOLLEY. *Ann. Pharm.* 106, 229; *J. pr. Chem.* 74, 448.

*Pichurimfett, Pichurimtalg* vid. pp. 44, 45.

*Sources.* In bay-berries (Marsson); in pichurim-beans (Sthamer); in cocoa-nut oil, inasmuch as this oil when saponified yields lauric acid. (Görgey, *Ann. Pharm.* 66, 298.)

*Preparation 1. From Bay-berries.* The pulverised berries are boiled three or four times with alcohol, pressed hot, and filtered as hot as possible. After 24 hours, the whole of the laurostearin separates from the filtrate as a whitish, yellow, curdy mass. The supernatant liquid still contains a very small quantity of laurostearin dissolved in a large quantity of green oil, from which it is difficult to separate. It is purified by washing with cold alcohol, recrystallisation from hot alcohol and pressure between bibulous paper. After this treatment, it still retains resin which may be separated by filtering the fused mass. (Marsson.)

*2. From Commercial Oil of Bay.* The oil is exposed to sunshine on porcelain plates covered with glass shades, whereupon the green colour soon disappears, and brown hard lumps of laurostearin separate

from the mass of fat melted by the sun's heat; these are separated by filtration, dissolved in alcohol and obtained of a pure white by evaporation or by precipitation with water. (Bolley.)

3. *From Pichurim-beans.* *Fabae pichurim major.* are exhausted with cold alcohol (which extracts volatile oil, pichurim-camphor, resin, a butyry fat and a brown colouring matter); and the exhausted beans are boiled with alcohol of 81 p. c. and pressed between hot plates. The expressed liquid, as it cools, deposits pale yellow laurostearin, only a small quantity of that substance remaining dissolved in the alcohol. It is purified by washing with cold alcohol, pressure, and recrystallisation from ether-alcohol. (Sthamer.)

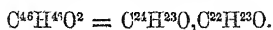
*Properties.* Snow-white, loosely coherent mass, consisting of needles arranged in stellate groups. (Marsson.) It crystallises from hot alcohol in stellate or arborescent groups of needles; from the ethereal solution by spontaneous evaporation in needles grouped in tufts. (Sthamer.) Melts between  $44^{\circ}$  and  $45^{\circ}$ , and on cooling solidifies in a non-crystalline brittle, friable mass, resembling stearin. (Marsson.) Melts between  $45^{\circ}$  and  $46^{\circ}$ , and solidifies at  $23^{\circ}$ . The solidification begins with the formation of small white scaly bodies with concave surfaces which afterwards run together. The whole then forms a white mass resembling stearin, and having its surface indented with small depressions of uneven surface. These hollow, when examined with a lens, are seen to contain needle-shaped crystals, arranged concentrically and radiating from the lowest point. The mass is brittle, odourless and friable. (Sthamer.)

				Marsson.	Sthamer.	
				a.	b.	
54 C	324	....	73.97	....	73.88	74.01
50 H	50	....	11.41	....	11.65	11.36
8 O	64	....	14.62	....	14.47	14.63
$C^{54}H^{80}O^8$				438	....	100.00
				100.00	....	100.00

a. From bay-berries; b. from pichurim-beans. Weltzien (*Syst. Zusammenst.* 559), gives the formula  $C^{54}H^{82}O^{10}$ , which, however, requires 71.05 per cent. C., and 11.4 H. See also Pohl (*Wien. Akad. Ber.* 10, 485).

*Decompositions.* Laurostearin burns with a bright flame (Sthamer). By dry distillation it yields acrolein (Marsson, Sthamer), a solid fat crystallisable from ether (Marsson), but no sebatic acid (Sthamer). — May be saponified with tolerable facility by *potash*, yielding a gelatinous soap. (Marsson.) It is decomposed by digestion with *basic acetate of lead*, with separation of glycerin. (Sthamer.) It dissolves with difficulty in cold, more readily in hot alcohol, whence it crystallises on cooling. Dissolves readily in ether.

## Laurostearone.



OVERBECK. *Pogg.* 85, 591.

### Laurone.

When laurate of lime is subjected to dry distillation in small



portions, laurostearone passes over in colourless drops which solidify in the neck of the retort. As soon as brown drops appear, the distillation is interrupted, and the resulting mass is crystallised from anhydrous alcohol, with addition of animal charcoal.

Dazzling white scales, melting at  $66^{\circ}$ , and then solidifying in a crystalline mass. Becomes strongly electric by friction.

						Overbeck.	
46 C .....	276	...	81.65	...	81.42	...	81.04
46 H .....	46	...	13.61	...	13.82	...	14.10
2 O .....	16	...	4.74	...	4.76	...	4.86
$C^{46}H^{46}O^2$ .....						338	...
						100.00	...
						100.00	...
						100.00	...

### *Appendix to Lauric Acid.*

### Bay-berry Camphor.



BONASTRE (1824). *J. Pharm.* 10, 32; abstr. *Repert.* 17, 190, *Br. Arch.* 13, 195.

DELFFS. *J. pr. Chem.* 58, 434; *Ann. Pharm.* 88, 354.

*Laurin, Lorbeer-campher.*—Discovered by Bonastre in bay-berries. The nearly inodorous pichurim-camphor, scarcely soluble in alcohol, which, according to Bonastre (*J. Pharm.* 11, 3), crystallises from the volatile oil of pichurim-beans, is, according to Gerhardt (*Traité*, 4, 309), perhaps bay-tree camphor.—Marsson (*Ann. Pharm.* 41, 329), by following Bonastre's directions, did not obtain any bay-tree camphor. Delffs, on the other hand, obtained it both from fresh and from old bay-berries.

*Preparation.* Shelled and pulverised bay-berries are boiled two or three times with alcohol of 85–90 per cent.; the solution is filtered at the boiling heat; the crystals of laurostearin, which separate from the filtrate after two or three hours, are removed by a second filtration, and the filtrate is left to evaporate in the air. The crystals which separate therein, together with oil-drops, are taken out from time to time, pressed between paper, to remove the gradually thickening oil, and crystallised from alcohol. (Delffs.)—Bonastre exhausts bay-berries with absolute alcohol; concentrates the extracts strongly till they separate into an oily and an alcoholic layer, and purifies the crystals which separate from both, by washing and recrystallisation from alcohol.

*Properties.* Dazzling white right rhombic prisms, with a dome resting on the acute edges, and dull or rough faces. (Delffs.) Needle-shaped rhombic octahedrons, having the angles of the base equal to  $60^{\circ}$  and  $120^{\circ}$ . (Bonastre.) Translucent, grates between the teeth, melts when heated (Bonastre). Tasteless and inodorous (Delffs); tastes bitter and sharp (Bonastre). Neutral.

						Delffs.	
44 C .....	264	...	77.20	.....	76.85	.....	76.85
30 H .....	30	...	8.77	.....	8.89	.....	8.89
6 O .....	48	...	14.03	.....	14.26	.....	14.26
$C^{44}H^{30}O^6$ .....						342	...
						100.00	.....
						100.00	.....

According to Delffs, it is  $C^{22}H^{15}O^3$ .

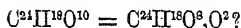
*Decompositions.* 1. Volatilises almost completely with resinous odour when heated, completely when thrown on red-hot coals. Resolved by dry distillation into water,—a yellow empyreumatic oil soluble in alcohol,—gases,—and a small residue of spongy charcoal.—2. Not decomposed by nitric acid.—3. Oil of vitriol colours it orange-yellow. (Bonastre.)

Insoluble in water. It imparts to boiling water a bitter taste (Bonastre); no taste (Delfs).—The alcoholic solution of bay-berry camphor does not precipitate neutral acetate of lead, or nitrate of silver. (Delfs.)

The camphor dissolves sparingly in cold alcohol, easily in boiling alcohol and in ether. (Bonastre.)

*Primary Nucleus*  $C^{24}H^{28}$ ; *Oxygen-nucleus*,  $C^{24}H^{18}O^8$ .

### Sapogenin.



FREMY. (1835.) *Ann. Chim. Phys.* 58, 102; *Ann. Pharm.* 15, 187; *J. pr. Chem.* 3, 393; abstr. *J. Pharm.* 20, 243.

QUEVENNE. *J. Pharm.* 23, 272.

ROCHLEDER & SCHWARZ. *Wien. Acad. Ber.* 11, 338.

A. OVERBECK. *N. Br. Arch.* 77, 134.

BOLLEY. *Ann. Pharm.* 30, 211, and 91, 117.

Fremy, in 1835, obtained his *esculic acid* by the decomposition of saponin from horse-chestnuts and from *Saponaria*. Quevenne regarded the *Acide polygalique modifié* obtained by the decomposition of senegin from *Polygala*, as allied to Fremy's acid, without, however, demonstrating the identity of the two. Both these bodies, together with Overbeck's *Saporetin*, are regarded as identical by Bolley, who unites them under the name *Sapogenin*.—Rochleder & Schwarz regard sapogenin from *Saponaria* as identical with quinin; but this view is rendered improbable by the more recent investigations of Hlasiwetz (*Ann. Pharm.* 111, 182).—We, here, with Bolley, regard the sapogenin resulting from decomposition as identical with the bodies obtained by Fremy and Quevenne; but we dissent from Bolley's view in regarding saponin as different from senegin, *Acide polygalique*.—The product which Fremy obtained by the second mode of preparation (p. 54) is perhaps different from sapogenin, and this may account for the difference between his statements and those of others. This view is supported by v. Payr's statement respecting the behaviour of saponin to hydrate of potash. (Kr.)

*Formation.* By treating saponin from horse-chestnuts or from *Saponarin* (Fremy), or senegin from *Polygala* (Quevenne), with dilute mineral acids. Grape-sugar is produced at the same time. (Rochleder & Schwarz; Overbeck.) Sapogenin is also produced from the saponin of horse-chestnuts by the action of potash-ley or of the electric current; but not from the saponin of *Saponaria*. (Fremy.)

*Preparation.* 1. An aqueous solution of saponin from horse-chestnuts is left in contact with cold hydrochloric acid for a long time, or with the boiling acid for a shorter time, and the precipitated sapogenin is washed with water. (Fremy.) Quevenne dissolves the sapogenin thus obtained in boiling alcohol of 40°, and evaporates the solution or precipitates it with water. Rochleder & Schwarz decompose saponin

by boiling with aqueous hydrochloric or sulphuric acid, dissolve the flocks in boiling acetic acid and mix the filtrate with cold water. Overbeck purifies the product by repeatedly digesting the alcoholic solution with animal charcoal, and leaves the filtrate to evaporate. Saponin may likewise be obtained from the decoction of *Senega* with previous preparation of senegin. (Bolley.)

2. Saponin from horse-chestnuts is treated with warm potash, whereupon sapogenin and a yellow colouring matter adhering to the saponin unite with the potash. By treating the product with weak alcohol, the latter compound may be separated, and the compound of sapogenin and potash obtained in crystals by leaving the solution to evaporate. This compound may be decomposed by precipitating its aqueous solution with acids. (Fremy.) By this process, pure sapogenin may be obtained from saponin of horse-chestnuts more readily than by 1. (Fremy.) See also, under *Saponin*, Rochleder & Schwarz's statements respecting its behaviour to potash.

*Properties.* Remains after the evaporation of its alcoholic solution in yellowish white, friable, irregular, amorphous lumps. (Quevenne.) Horny laminae which may be rubbed to a white powder. (Overbeck.) According to Fremy sapogenin either from horse-chestnuts or from *Saponaria* may be crystallised from alcohol. Tasteless (Fremy); the taste is but faint at first, but afterwards very bitter. (Quevenne.) The alcoholic solution reddens litmus. (Quevenne.)

Calculation according to															
Fremy.				Rochleder & Schwarz.											
				a.			b.								
52 C.....	312	...	56.73	...	12 C.....	72	...	63.16	...	60 C.....	360	...	67.41		
46 H.....	46	...	8.36	...	10 H.....	10	...	8.77	...	46 H.....	46	...	8.61		
24 O.....	192	...	34.91	...	4 O.....	32	...	28.07	...	16 O.....	128	...	23.98		
<hr/>															
$C^{52}H^{46}O^{24}$ .....				550	...	$C^{12}H^{10}O^4$ .....		114	...	$C^{60}H^{46}O^{16}$ .....		534	...	100.00	
<hr/>															
Overbeck.						Bolley.									
18 C.....						108	...	63.53		...	24 C.....		144	...	59.51
14 H.....						14	...	8.23		...	18 H.....		18	...	7.13
6 O.....						48	...	28.24		...	10 O.....		80	...	33.06
<hr/>															
$C^{18}H^{14}O^6$ .....						170	...	100.00		...	$C^{24}H^{18}O^{10}$ .....		242	...	100.00
<hr/>															
Fremy.				Rochleder & Schwarz.				Overbeck.		Bolley.					
a.		b.		a.		b.		at 100°.		a.		b.			
														mean.	
C.....	56.79	...	56.43	...	63.35	...	67.04	...	63.30	...	59.20	...	60.03		
H.....	8.35	...	8.64	...	8.57	...	8.88	...	8.76	...	7.70	...	7.60		
O.....	34.86	...	34.93	...	28.08	...	24.08	...	27.94	...	33.10	...	32.37		
<hr/>															
100.00		100.00		100.00		100.00		100.00		100.00		100.00			

a. From horse-chestnuts; b. from *Saponaria* (Fremy).—a. dried for several hours between 120° and 125°; b. for twenty-four hours at 100°; both products from *Saponaria*. (Rochleder & Schwarz).—Bolley analysed sapogenin, a. from *Senega*, b. from *Saponaria*.—The great discrepancies between the analyses arise from the partial alteration of sapogenin in drying. It should therefore be dried in a stream of carbonic acid. (Rochleder, *Wien. Akad. Ber.* 16, 1).

*Decompositions.* 1. In drying (vid. sup.).—2. When heated it does not melt till it begins to decompose; it does not yield any peculiar products

by dry distillation. (Fremy.)—3. In contact with *oil of vitriol* it turns violet, and imparts a faint violet tint to the oil of vitriol itself. (Quevenne.) It dissolves in oil of vitriol with red-brown colour; in less concentrated sulphuric acid with red colour. (Rochleder & Schwarz.)—4. With *nitric acid*, it forms a brown resin and red vapours. (Fremy.)—5. It appears to be somewhat altered by prolonged boiling with dilute acids. (Bolley.)

*Combinations.* Sapogenin is nearly insoluble in boiling water. (Fremy.) When left in contact with water for a considerable time, it does not swell up, but dissolves slightly, so that the solution precipitates metallic salts. (Quevenne.)

It unites with *bases*, without losing water. The resulting compounds, Fremy's *esculates*, are decomposed by carbonic acid.

The compounds with *Ammonia*, *Potash*, and *Soda* are soluble in water, and solidify to a jelly when their aqueous solutions are evaporated, but separate from a mixture of 1 pt. water and 2 pts. alcohol in beautiful pearly laminae. They contain 1 at. base to 2 at. sapogenin. (Fremy.) Alcoholic sapogenin neutralized with potash-ley leaves, when evaporated, an amorphous, white, very bitter mass, not containing any crystals. (Quevenne.) Sapogenin forms with the alkalis very bitter compounds, which are soluble in water. (Rochleder & Schwarz.) Gelatinous sapogenin dissolves readily in aqueous alkalis, but after drying it dissolves but imperfectly even when boiled in the liquid. (Overbeck.)

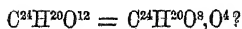
With *Baryta*, *Strontia*, and *Lime*, sapogenin forms compounds insoluble in water and in alcohol of 40°, but soluble in dilute alcohol. (Fremy.) Alcoholic sapogenin precipitates baryta- and lime-salts, but not *hydrochlorate of magnesia*. (Quevenne.) Bolley's sapogenin likewise precipitates baryta-salts.

With *Lead-oxide* or *Cupric oxide* sapogenin forms compounds insoluble in water. (Fremy.) Alcoholic sapogenin precipitates *sulphate of copper*, *neutral and basic acetate of lead*, *ferrous and ferric sulphates*, *nitrate of silver* and *bichloride of platinum*. (Quevenne.) Sapogenin prepared from *Saponaria* or from *Senega*, precipitates neutral acetate of lead but slightly; basic acetate of lead, ferric salts, silver salts, and *mercuric salts* more copiously. (Bolley.) Overbeck's sapogenin does not precipitate an alcoholic solution of neutral acetate of lead.

Sapogenin dissolves very readily in *alcohol*, but is insoluble in *ether*. (Fremy.) From aqueous *tannic acid* it throws down a small precipitate. (Quevenne.)

*Primary Nucleus*  $C^{24}H^{28}$ ; *Oxygen-nucleus*  $C^{24}H^{20}O^8$ ?

### Picrolichenin.



ALMS. (1832.) *Ann. Pharm.* 1, 61.

GREGORY. *J. Pharm.* 21, 314.

A. VOGEL, jun., & WUTH. *N. Jahrb. Pharm.* 8, 201; *N. Br. Arch.* 95, 67; *J. pr. Chem.* 72, 272.

*Occurrence.* In *Variolaria amara*.

*Preparation.* The lichen is distilled with rectified spirit (if it remains in contact with the liquid for too long a time, it undergoes alteration, and a brown mass is obtained, Vogel & Wuth); the extract is evaporated to a syrup, and left at rest; and the crystals, which separate after fourteen days, are purified by washing with weak potash-ley, and repeated crystallisation from alcohol. (Alms.) A pound of the lichen yields half an ounce of picrolichenin.

*Properties.* Colourless, transparent, highly lustrous, rhombic octahedrons. Melts a little above the melting point of sulphur, and solidifies to a transparent brittle mass on cooling. Not volatile without decomposition. Sp. gr. 1.176. Inodorous, but has a strongly bitter taste. The solutions redden litmus.

				Vogel & Wuth.	
				<i>mean.</i>	
24 C .....	144	....	55.38	.....	55.85
20 H .....	20	....	7.69	.....	7.78
12 O .....	96	....	36.93	.....	36.37
<hr/>				<hr/>	
$C^{24}H^{20}O^{12}$ .....	260	....	100.00	.....	100.00

According to Vogel & Wuth it is perhaps isomeric with senegin.

*Decompositions.* 1. Picrolichenin heated considerably above its melting point, decomposes, giving off white fumes, which irritate the organs of respiration, and leaves a loose, shining charcoal.—2. *Chlorine-water* colours it sulphur-yellow.—3. The solutions in *ammonia* and in *potash-ley* turn red on exposure to the *air*; and on addition of acids, deposit altered picrolichenin which has lost the whole or nearly the whole of its bitterness. (Alms. *vid. inf.*)

*Combinations.* Picrolichenin is insoluble in cold *water*, but dissolves slightly in boiling *water*, without separating again on cooling.—Strong *nitric acid* dissolves it in small quantity at the boiling heat, without colouring or evolution of gas. *Oil of vitriol* forms with picrolichenin a colourless solution, which becomes turbid when mixed with *water* or exposed to the *air*.

With *Ammonia*.—Aqueous ammonia dissolves picrolichenin, out of contact with *air*, forming a solution colourless at first, but afterwards becoming saffron-yellow, which after some time deposits very brilliant, transparent, tasteless, crystalline tufts. These crystals effloresce on drying, and melt at  $50^{\circ}$  to a cherry-red resin, which is difficult to dry, gives off ammonia at a higher temperature, is insoluble in *water*, but dissolves with cherry-red colour in ammonia, potash, and alcohol.—The crystals dissolve sparingly in *water*, easily in ammonia, potash, and alcohol. (Alms.)

Picrolichenin dissolves very easily in aqueous *potash* to a frothy liquid; sparingly in *carbonate of potash*. (Alms.)

It dissolves easily in *bisulphide of carbon*, also in warm *acetic acid*, crystallising out on cooling, and being precipitated by *water*.—It dissolves readily in *alcohol*, and is precipitated therefrom by *water*; easily in *ether* and in volatile oils after prolonged boiling, also in *fixed oils*. (Alms.)

Oxygen-nucleus  $C^{24}H^{12}O^{16}$ .

# Physodin.

$C^{24}H^{12}O^{16}$ .

GERDING. *N. Br. Arch.* 87, 1.

*Occurrence.* In *Parmelia physodes*.

*Preparation.* The lichen air-dried and cut in pieces is macerated for several days with ether; the ethereal extract is evaporated; and the residual white powder is purified by washing with alcohol and repeated crystallisation from absolute alcohol.

*Properties.* White, loosely coherent mass, appearing when magnified 120 times, to consist of four-sided truncated prisms; if obtained from the alcohol solution by spontaneous evaporation, it forms crystals  $2\frac{1}{2}$  lines long. Melts at  $125^{\circ}$ . Neutral to vegetable colours.

										Gerding, mean. at $100^{\circ}$ .
a.										
24 C .....	144	....	50.70	....	20 C .....	120	....	49.51	.....	49.75
12 H .....	12	....	4.28	....	10 H .....	10	....	4.13	.....	4.63
16 O .....	128	....	45.07	....	14 O .....	112	....	46.36	.....	45.62
$C^{24}H^{12}O^{16}$ ....	284	....	100.00	....	$C^{20}H^{10}O^{14}$ ....	242	....	100.00	.....	100.00

Gerding, by an inexact calculation, obtained the formula  $C^{20}H^{10}O^{15}$ , which requires 47.8 per cent. C., 4.4 H., and 47.8 O. This formula is resolved by Weltzien into  $C^{20}H^{10}O^{15} + 3$  aq. (*Syst. Zusammenst.* 523.)

*Decompositions.* 1. Physodin, when heated to  $125^{\circ}$ , is converted into a dark rose-coloured product, Gerding's physodein, which contains 51.08 p. c. C., 4.00 H., and 44.82 O., according to Gerding,  $C^{20}H^{10}O^{15}$ , and is produced from physodin by loss of water. This formula agrees with that of physodin;  $C^{24}H^{12}O^{16}$  requires 52.36 p. c. C., 4.00 H. (Kr.) — 2. Oil of vitriol dissolves physodin with violet and afterwards with deep rose-red colour, and water then precipitates bluish violet flocks. — 3. By nitric acid it is converted into oxalic acid with evolution of nitrous gas.

*Combinations.* Physodin behaves to water like a resin, and is (? not) wetted by it. It is not altered by dilute acids.

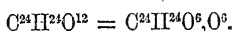
It dissolves easily in warm aqueous ammonia, forming a yellow solution, which becomes reddish on exposure to the air. When exposed to ammonia vapours, it assumes a chrome-yellow colour, and afterwards brown-red in contact with the air. — In carbonate of ammonia it dissolves slightly at mean temperatures, easily on boiling; in potash-ley instantly, with yellow colour. Acids precipitate from these solutions light yellow or reddish flocks; the potash-solution yields a dingy yellow precipitate with chloride of barium. The alcoholic solution of physodin is not precipitated by chloride of barium, but it yields with acetate of lead a pale yellow precipitate, soluble in potash-ley, with

*sulphate of copper* a pale green; and with *nitrate of silver* a brown-red precipitate.

It is insoluble in *alcohol* of 80 p. c., but dissolves in boiling absolute alcohol. It is insoluble in *ether* and in *acetic acid*.

*Primary Nucleus*  $C^{24}H^{30}$ ; *Oxygen-nucleus*  $C^{24}H^{24}O^6$ .

### Leucic Acid.



CAHOURS. *Compt. rend.* 27, 368.

A. STRECKER. *Ann. Pharm.* 68, 55; *Lehrbuch*. 3 Aufl. 200.

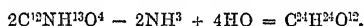
GÖSSMANN. *Ann. Pharm.* 91, 135.

WAAGE. *Ann. Pharm.* 118, 295.

THUDICHUM. *Chem. Soc. Qu. J.* 14, 307.

$C^{24}H^{24}O^{12}$  from its analogy with lactic acid (xi. 472), which, however, according to more recent investigations, appears to be  $C^6H^6O^6$  (Kr.) The experiments of Waage and Thudichum tend rather to show that leucic acid is  $C^{12}H^{12}O^6$ .

*Formation.* 1. Leucine, dissolved in water, is converted, by the action of oxidising agents, or even on standing, into a peculiar acid  $C^{12}H^{12}O^6$ . (Cahours.) When nitric oxide gas is passed through a solution of leucine in strong nitric acid [or nitrous acid through a solution of leucine in warm water (Thudichum), or water slightly acidulated with nitric acid (Waage)], nitrogen is evolved, and oily leucic acid, soluble in ether is produced (Strecker):



2. When chlorine gas, not in excess, is cautiously passed through a solution of leucine in caustic soda, leucic acid is formed and may be separated from the mixture in the same manner as benzoglycollic acid (xii, 64) from hippuric acid. (Gössmann.)

¶. *Preparation.* Purified leucine\* is dissolved in boiling water slightly acidulated with nitric acid, and nitrous acid gas is passed through the warm solution as long as nitrogen continues to escape; the liquid, which turns brown and gradually deposits brown flakes, is left to cool,

\* The leucine used in the preparation was prepared by Hinterberger's method (*Ann. Pharm.* 91, 135), as modified by Schwanert (*ibid.* 102, 221), viz., by boiling ox-horn for some time with sulphuric acid; adding milk of lime in excess, filtering, boiling again, and precipitating the lime with oxalic acid; decolorising the filtrate by adding sulphate of copper, and precipitating the copper with sulphuretted hydrogen; then concentrating the filtrate, and leaving it to crystallise. The leucine thus obtained was further purified by repeated crystallisation from water and weak spirit, finally decolorised by boiling it with a small quantity of hydrated oxide of lead, and precipitating the dissolved lead with sulphuretted hydrogen; the solution was then evaporated and the leucine once more crystallised from dilute alcohol. The product was quite colourless, but left 2 per cent. of ash when burnt, and still contained a trace of sulphur. (Waage.)

then agitated several times with ether; and the ethereal extracts are evaporated. The residue is a brown oily liquid not miscible with water, which gradually solidifies to a radio-crystalline mass. The aqueous solution freed from leucic acid by repeated agitation with ether, left on evaporation a considerable quantity of nitro-leucic acid. — To purify the crude leucic acid thus obtained, it is dissolved in a large quantity of water (a smaller quantity dissolves it but imperfectly); the boiling liquid is mixed with an aqueous solution of acetate of zinc; and the precipitated leucate of zinc is washed on the filter with water (which dissolves but a small quantity of it), purified by recrystallisation from alcohol, then suspended in water, and decomposed by sulphuretted hydrogen. The filtered solution is but very slightly coloured, and when evaporated to a syrup and left to stand, yields leucic acid in colourless needles. If, on the other hand, the zinc-salt be suspended in alcohol and decomposed by sulphuretted hydrogen, the acid is obtained in hard, brittle prisms. (Waage.)

2. Thudichum passes nitrous acid gas through a warm aqueous solution of leucine; evaporates with addition of leucine to neutralise the free nitric acid, and prevent it from oxidising the leucic acid; agitates the syrupy residue with ether (or extracts the leucic acid from the aqueous solution by agitation with ether, without previous evaporation; in which case, however, the treatment with ether must be repeated a great number of times);—and purifies the crude leucic acid from adhering brown oil, either by solution in cold water, filtration and recrystallisation, or by strongly pressing the coloured crystals between bibulous paper,—or by precipitating the aqueous solution with acetate of lead, decomposing the washed precipitate with sulphuretted hydrogen, and evaporating the filtrate, either over the water-bath at a very moderate heat, or over sulphuric acid.

*Properties.* Colourless needles. (Strecker.) Needles or hard, brittle prisms, of the right or oblique prismatic system, according to the mode of preparation. (Waage, *vid. sup.*) Radiary groups of needles, having a mother-of-pearl lustre, with a beautiful variety of concentric markings, like those of some kinds of larch-agaric. (Thudichum.) Heavier than water. Cuts like hard soap, almost like stearic acid. (Thudichum.) Has an acid taste, and reddens litmus (Thudichum); bitter taste, and strong acid reaction (Waage). Melts below  $100^{\circ}$  and solidifies on cooling. (Thudichum.) Melts at  $73^{\circ}$ , and sometimes solidifies at a few degrees below the melting point, sometimes remains liquid even when cooled to  $0^{\circ}$ . (Waage.)

				Waage. Thudichum. mean.		
12 C .....	72	...	54.54	.....	54.3	..... 53.57
12 H .....	12	...	9.09	.....	9.1	..... 8.73
6 O .....	48	...	36.37	.....	36.6	..... 37.70
<hr/>				<hr/>		
$C^{12}H^{12}O^6$ .....	132	...	100.00	.....	100.0	..... 100.00

The loss of carbon in Thudichum's analyses arose from partial decomposition.

*Decompositions.* 1. Leucic acid volatilises at  $100^{\circ}$ , apparently without decomposition. If placed on a watch-glass and heated over the water-bath, the sides of the glass become fringed with crystals of the sublimed acid, which dissolve easily in water, leaving, however, a



few flocks, probably consisting of the anhydride. The mass which remains in the middle of the watch-glass is syrupy, dissolves in water only after prolonged boiling, but is easily soluble in alcohol and ether; it probably consists of *leucic anhydride*; but whether corresponding to lactic anhydride (xi. 501) or to lactide, is at present undetermined. (Waage.) The acid heated for some time in the water-oven continually gives off acid-smelling vapours, and does not afterwards solidify on cooling, but remains in the form of an uncrystallisable, dark brown smeary syrup; the anhydride, which has a very disagreeable odour, remains unchanged, even when left over oil of vitriol for weeks, and is nearly insoluble in water, separating from it like an oil and sinking to the bottom. A small quantity of this insoluble compound is likewise formed when the aqueous solution, even if dilute, is heated to the boiling point or evaporated. The formation of this insoluble compound renders the preparation of pure salts of leucic acid rather difficult, and has doubtless also given rise to the statement sometimes made that leucic acid is uncrystallisable. (Thudichum.) — 2. Leucic acid strongly heated in the *air*, gives off thick fumes and blackens, then takes fire and burns with a yellow smoky flame, leaving a small quantity of charcoal, which is quickly and easily consumed. (Thudichum.)

*Combinations.* Very soluble in *water*. (Waage, Thudichum.) Difficultly soluble. (Strecker.) Strecker's acid was, perhaps, partially converted into the insoluble compound above mentioned. A small piece placed on water dissolves rapidly, producing curious currents of diffusion. The solution has an agreeably acid taste, reddens litmus, and decomposes carbonates.

*Leucates.*—Leucic acid forms crystallisable salts (Strecker, Thudichum), most of which have the composition  $C^{12}H^{11}MO^6$ . An acid silver-salt appears, however, to exist, which may be either  $C^{12}H^{11}AgO^6$ ,  $C^{12}H^{12}O^6$ , or  $C^{24}H^{23}AgO^6$ ; but as no acid leucate of any other base has been produced, the 12-carbon formula of the acid must be regarded as the more probable—a conclusion also pointed out by the formation of the acid from leucine. The salts are for the most part obtained by boiling the aqueous solution of the acid with the corresponding carbonates. (Thudichum.)—They are less soluble than the lactates in water, more soluble in alcohol. (Waage.)

*Leucate of Ammonia.*—The acid slightly supersaturated with ammonia, and evaporated, leaves a thick homogeneous residue, in which no trace of crystallisation can be observed, even after drying for several weeks over oil of vitriol. (Thudichum.)

*Leucate of Soda.*—The aqueous acid neutralised with carbonate of soda and evaporated, leaves a syrupy residue covered with a crystalline crust. When this syrup is left over oil of vitriol, crystals form in it, which, under the microscope, exhibit a characteristic tub-shape, with rhombic plates interspersed here and there. (Thudichum.)

*Leucate of Baryta*,  $C^{12}H^{11}BaO^6$ .—Obtained by digesting the aqueous acid with carbonate of baryta. (Waage, Thudichum.) It dissolves with moderate facility in warm water and dilute alcohol, and separates from boiling alcohol in beautiful colourless, silky, laminar crystals,

which, like most leucates, retain something of the appearance of leucine. (Waage.) Thudichum obtained it by evaporation in crystalline crusts, which remained yellow even after pressing and drying. It is anhydrous, and gives by analysis 38.6 p. c. baryta, the formula requiring 38.4 p. c. (Waage.)

By evaporating two equal quantities of the acid, one of which had been neutralised with carbonate of baryta, a smeary semi-solid mass was obtained, apparently consisting of a mixture of the neutral salt with free leucic acid. (Thudichum.)

*Leucate of Lime.*  $\text{C}^{12}\text{H}^{11}\text{CaO}^6$ .—An aqueous solution of the acid neutralised with chalk or milk of lime and left to evaporate, yields the lime-salt in fine needles, easily soluble in water and in alcohol. (Waage.) Thudichum obtained it in non-crystalline crusts, which gave by analysis 12.68 and 12.78 p. c. lime (calc. 13.24 p. c.).

*Leucate of Magnesia.*—Sparingly soluble in water, deposited in crusts on evaporation. (Thudichum.)

*Leucate of Zinc.*—Obtained by neutralising the dilute acid at the boiling heat with carbonate of zinc, and filtering at the same temperature. If the solution of leucic acid is not exceedingly dilute, a thick froth containing undissolved leucate and carbonate of zinc is formed at the top of the liquid, which requires repeated boiling with water to dissolve it. The latest solutions are the purest and least coloured. The solution deposits a thin crust on cooling. Evaporated over the water-bath, it soon becomes covered with a crust, and on cooling deposits bulky masses of needles, which must be separated by filtration, pressed between bibulous paper, and dried by exposure to the air or over the water-bath. The best crystals are obtained from a solution containing excess of leucic acid. (Thudichum.) For Waage's mode of preparation, see page 59.

Snow-white, with splendid silky lustre; exhibits under the microscope the appearance of masses of needles. (Thudichum.) Extremely light scales, of dazzling whiteness and silky lustre. (Waage.) Sparingly soluble even in boiling water, less in cold water. (Thudichum.) Dissolves in 300 pts. water at  $16^\circ$ , and in 204 pts. boiling water, more soluble in alcohol. (Waage.) The air-dried salt gives off 5.1 p. c. water (1 at.) at  $100^\circ$  (Waage); gives off half its water at  $100^\circ$ , but requires a temperature of  $120^\circ$ – $130^\circ$  to dry it completely. (Thudichum.)—Sulphuretted hydrogen precipitates the zinc completely (Waage), only a portion even after repeated saturation of the solution with the gas. (Thudichum.)

at $120^\circ$ – $130^\circ$			Thudichum. mean.	Air-dried.			Waage.
12 C .....	72.0 ....	44.01 ....	43.87 ....	12 C.....	72.0 ....	41.72	
11 H .....	11.0 ....	6.72 ....	6.89 ....	11 H ....	11.0 ....	6.37	
Zn .....	32.6 ....	19.92 ....	20.10 ....	Zn ....	32.6 ....	18.89 ....	18.79
6 O .....	48.0 ....	29.26 ....	29.14 ....	6 O .....	48.0 ....	27.81	
				HO .....	9.0 ....	5.21 ....	5.10
$\text{C}^{12}\text{H}^{11}\text{ZnO}^6$ ....			163.6 ....	100.00 ....	100.00 ....	+ Aq ....	172.6 .... 100.00

*Leucate of Lead.*—On adding acetate of lead to a solution of leucic acid or a leucate, a copious white precipitate is produced, which is flaky, and, on boiling, dissolves almost entirely in the liquid. Any portion remaining undissolved melts into a white mass, which is soft like

resin while warm, but becomes brittle and hard on cooling. This substance is insoluble in water and alcohol, even on boiling, and seems to be a basic salt.

If the solution of lead is added to a boiling solution of the acid, no precipitate ensues, acid vapours are evolved, and the liquid becomes milky on cooling. In a short time, it deposits the lead-salt as a light, granular, white mass, which, under the microscope, appears to be made up of a multitude of strongly refracting spherical masses, of the size of human blood-corpuscles. This salt is more easily soluble in an excess of the acetate than in water. It is easily soluble in spirit of wine, particularly in boiling spirit. Even in these solutions, basic salts are easily formed. The addition of water to these solutions produces a precipitate. (Thudichum.)

*Leucate of Cobalt.* — The dilute aqueous acid boiled with excess of carbonate of cobalt, then filtered and evaporated, deposits light crusts of a pink colour while moist, but of a very pale rose-colour or almost white when dry. The salt is but sparingly soluble in cold water, and not much more soluble at the boiling heat. It crystallises in needles, which, under the microscope, appear to be arranged in globular masses.

				Thudichum.
				mean.
12 C.....	72	...	44.85	..... 44.82
11 H .....	11	...	6.85	..... 6.77
Co .....	30	...	18.38	..... 18.38
6 O.....	48	...	29.92	..... 30.03
$C^{12}H^{11}CoO^6$ .....				161 .... 100.00 ..... 100.00

*Leucate of Copper.* — When a dilute aqueous solution of leucic acid is treated with a dilute solution of ammonio-sulphate of copper, the colour of the copper-salt changes to light green. On boiling the liquid, it becomes paler, and, on cooling, deposits light green granules of leucate of copper. Under high powers of the microscope, these granules appear as balls, formed by a radiary arrangement of needles (Thudichum.) — A solution of leucic acid mixed with acetate of copper forms a green flocculent precipitate, very sparingly soluble in water, even at the boiling heat, but easily crystallised from boiling alcohol, from which it separates in very beautiful light blue, shining, bulky scales, which do not undergo any diminution in weight at  $100^{\circ}$ . (Waage.)

				Waage.	Thudichum.
12 C.....	72.00	...	44.25	.... 44.5	
11 H.....	11.00	...	6.76	.... 6.9	
Cu .....	31.68	...	19.49	.... 19.3	.... 18.56
6 O.....	48.00	...	29.50	.... 29.3	
$C^{12}H^{11}CuO^6$ .....				162.68 .... 100.00 .... 100.00	

*Mercurous Leucate.* — When to a solution of leucic acid a solution of mercurous nitrate is added, a slight turbidity ensues. The addition of carbonate of soda produces a copious reddish-white precipitate, which, on boiling, becomes red, then dull grey, and deposits metallic mercury at the bottom of the tube. (Thudichum.)

*Mercuric Leucate* may be prepared:—*a.* Directly, by dissolving freshly-precipitated moist mercuric oxide in aqueous leucic acid. A flaky precipitate gradually ensues, which, on heating, becomes red and granular, and adheres to the sides of the glass. On cooling, a new precipitate, consisting of whitish globules, is deposited.—*b.* By adding mercuric nitrate to an aqueous solution of leucic acid. A whitish-red precipitate is formed, which dissolves on boiling, and, on cooling, is again deposited in reddish granules.—*c.* By adding the mercurial solution to the leucate of an alkali.

The leucates of both oxides of mercury have a great tendency to become reduced. The mercuric salt easily passes into the mercurous salt. The mercuric salt, moreover, has a great tendency to become basic and insoluble. (Thudichum.)

*Leucate of Silver.*—*a. Neutral.*—Obtained by adding nitrate of silver to the solution of the acid neutralised with ammonia, or by boiling the acid with oxide of silver, and may be rendered quite colourless by recrystallisation from boiling water, in which it is moderately soluble. It is anhydrous. (Waage.) Nitrate of silver added to a warm solution of leucate of ammonia, potash or soda, forms a copious white crystalline precipitate, which increases as the liquid cools, and blackens if left in the mother-liquor. (Thudichum.)

<i>Dried over oil of vitriol.</i>				<i>Waage. Thudichum.</i>	
12 C .....	72	...	30.13		
11 H .....	11	...	4.60		
Ag .....	108	...	45.19	...	45.2
6 O .....	48	...	20.08	...	44.14
<hr/>					
$C^{12}H^{11}AgO^8$ .....	239	...	100.00		

The salt, dried over the water-bath below  $100^{\circ}$ , became brown and continued to lose weight. (Thudichum.)

*Acid salt.*—A hot dilute solution of leucic acid decomposes recently-precipitated carbonate of silver with effervescence. The excess of carbonate of silver and the undissolved portion of the leucate become blackish-grey, but the acid is not entirely neutralised. The hot filtrate forms no deposit on cooling. The attempt to evaporate it over the water-bath produces a black precipitate of reduced silver. It must, therefore, be evaporated in vacuo over oil of vitriol. After prolonged standing, a few crystals, of a glassy lustre and appearing under the microscope as groups of rhombic plates, are deposited at the margin of the dish. The liquid then becomes covered with a pellicle, and evaporation is impeded. At a later stage, conglomerates of needles are deposited, which, when carefully dried over sulphuric acid in vacuo, appear a little blackened, like most silver-salts, but are not decomposed. Silver by analysis 26.97 p. c.; the formula requires 29.1 p. c. (Thudichum.)

Leucic acid is soluble in *alcohol* and in *ether*. (Strecker, Thudichum, Waage.) ¶.

*Appendix to Compounds containing 24 atoms of Carbon.***Panaquilone.**

S. GARRIQUES. *Ann. Pharm.* 90, 231; *Pharm. Centr.* 1854, 721; *J. pr. Chem.* 63, 97.

*Occurrence.* In the root of American ginger, *Panax quinquefolius*.

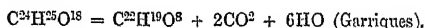
*Preparation.* The aqueous infusion of the root precipitated in the cold is freed from albumin by heating; the filtrate is evaporated to a syrup, and precipitated with a strong solution of sulphate of soda; and the brown, glutinous precipitate is washed with the same solution and heated with absolute alcohol. Panaquilone then dissolves, remains behind when the alcohol is distilled off, and may be purified by solution in water, treatment with animal charcoal, evaporation, and re-solution in absolute alcohol.

*Properties.* Amorphous, yellow powder, having a bitter-sweet taste. Free from nitrogen.

								Garriques. mean at 100°.	
a.				b.					
24 C .....	144	...	46·01	...	40 C .....	240	...	45·98	..... 45·94
25 H .....	25	...	7·98	...	42 H .....	42	...	8·04	..... 8·05
18 O .....	144	...	46·01	...	30 O .....	240	...	45·98	..... 46·01
C <sup>24</sup> H <sup>25</sup> O <sup>18</sup> .....	313	...	100·00	...	C <sup>40</sup> H <sup>42</sup> O <sup>30</sup> .....	522	...	100·00	..... 100·00

a. According to Garriques.

*Decompositions.* 1. When heated, it melts, decomposes, and burns away without residue.—2. It dissolves in oil of vitriol, with fine purple-red colour, and water added to the solution throws down white panacone; hydrochloric and nitric acids, with aid of heat, produce the same transformation. In this reaction, carbonic acid is evolved, but no sugar is formed:



*Combinations.* Panaquilone dissolves readily in water. The solution is not precipitated by acids, mercuric chloride, or bichloride of platinum; it is coloured brown by alkalis.

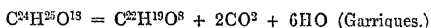
Panaquilone dissolves easily in alcohol, but is insoluble in ether. From its aqueous solution it is precipitated by tannic acid.

**Panacone.**

GARRIQUES. *Ann. Pharm.* 90, 233; *J. pr. Chem.* 63, 97; *Pharm. Centr.* 1854, 321.

*Formation and Preparation.* When panaquilone is dissolved in oil of vitriol, or when its aqueous solution is heated with hydrochloric or

nitric acid, it is resolved into panacone, which separates out, and carbonic acid and water:



*Properties.* White tasteless powder, composed of microscopic crystals.

Calculation according to Garriques.				Garriques.			
22 C.....	132	...	61.43	.....	59.22	...	61.06
19 H.....	19	...	8.83	.....	8.93	...	8.85
8 O.....	64	...	29.74	.....	31.85	...	30.09
<hr/>							
$\text{C}^{22}\text{H}^{19}\text{O}^8$ .....	215	...	100.00	.....	100.00	...	100.00

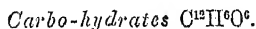
The formula, which does not accord with the principles of this Work, may perhaps be made correct by doubling (Kr.).

Panacone melts when *heated*, and burns with flame. — Hot concentrated *nitric acid* converts it into oxalic acid.

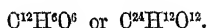
It is insoluble in *water*, dissolves, with purple colour, in *oil of vitriol*, and is precipitated therefrom by water. — It is not altered by *alkalis*. — It is soluble in *alcohol*, but insoluble in *ether*.

## Carbo-hydrates or Saccharoidal Substances.

The bodies belonging to this group cannot, with certainty, be arranged in the general system. The order, in which they are here described, is such that a compound, in which (independently of crystallisation-water) the sum of the hydrogen and oxygen-atoms is expressed by a smaller number, takes precedence of one in which that sum is larger. The compounds derived from these carbo-hydrates (mannitan, xyloidin, sulphosaccharic acid, &c.), are likewise arranged independently of the nucleus-system, being placed immediately after the primary compound. Moreover, as the compounds containing 12 atoms of carbon have already been described (vol. xi.), it is a matter of necessity to treat all carbo-hydrates in connection with the 24-carbon compounds, without entering upon the question whether their molecule really contains 12 or 24 at. C. (Kr.).

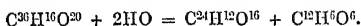


### Phloroglucin.



HLASIWETZ. *Wien. Akad. Ber.* 17, 382. *J. pr. Chem.* 67, 105; abstr. *Ann. Pharm.* 96, 118; *Chem. Gaz.* 1856, 81; *Lieb. Kopp. Jahresber.* 1855, 700. — *Wien. Akad. Ber.* 36, 401; *Ann. Pharm.* 112, 96; *J. pr. Chem.* 78, 257; abstr. *Chem. Centr.* 1860, 132; *Rép. Chim. pure*, 2, 139; *Kopp's Jahresber.* 1859, 524. — *Wien. Akad. Ber.* 43, 451; *Ann. Pharm.* 119, 199; *Rép. Chim. pure*, 1861, 459.

*Formation.* 1. Phloretin boiled with potash-ley is resolved into phloretic acid and phloroglucin.—2. Quercetin, under the same circumstances, is resolved into quercetic acid and phloroglucin:



*Preparation.* 1. See xii, 307. The mixture of phloroglucin and carbonate of potash obtained as there described (whence alcohol does not extract any phloroglucin) from which all the phloretate of potash has been extracted by alcohol, is dissolved in water; dilute sulphuric acid is added in slight excess; and the mass is evaporated to dryness over the water-bath, and then well boiled with alcohol (better with ether-alcohol). The alcohol is distilled off and the residue left to crystallise, whereby strongly-coloured crystals are obtained, the mother-liquor also yielding an additional quantity. They are dissolved in water, and the solution is mixed with acetate of lead (which produces no precipitate), and saturated with sulphuretted hydrogen, the precipitated sulphide of lead carrying down nearly the whole of the colouring matter, so that the crystals which afterwards separate have only a yellowish tint. By recrystallisation from ether and afterwards from water, they may be obtained quite colourless.

2. Quercetin is added to a hot concentrated solution of 3 pts. hydrate of potash, the liquid evaporated down at the boiling heat, and the residue further heated, till a sample of it taken out no longer yields a flocculent precipitate with hydrochloric acid, and quickly assumes a deep red colour when dissolved in water. The whole is then immediately dissolved in water, the solution which instantly turns red is neutralised with hydrochloric acid, and the flocks (of alpha-quercetin and undecomposed quercetin) which are deposited from the liquid on standing and cooling, are separated by filtration. The filtrate is evaporated to dryness, the residue exhausted with alcohol; the alcohol distilled off from the brown tincture; the residue dissolved in water, and mixed with acetate of lead, whereby quercetate of lead is precipitated, while phloroglucin remains in solution. The latter is obtained in the crystalline state by removing the lead from the filtrate with sulphuretted hydrogen and quickly evaporating, and is purified by recrystallisation with help of animal charcoal.

*Properties.* Phloroglucin separates from absolute ether in anhydrous crystals (see hydrated phloroglucin). It is sweeter than common sugar. Neutral. Permanent in the air at ordinary temperatures and at  $100^\circ$ . Melts at about  $220^\circ$ . Sublimes partially without particular odour, and solidifies on cooling.

						Hlasiwetz.	
						mean.	
<i>Anhydrous at <math>100^\circ</math>.</i>						a.	b.
12 C	72	57.13	57.00	56.93			
6 H	6	4.76	5.08	4.98			
6 O	48	38.11	37.92	38.09			
$C^{12}H^6O^6$	126	100.00	100.00	100.00			

a. Prepared from phloretin; b. from quercetin.

*Decompositions.* Ammoniacal phloroglucin shaken up with air,

becomes red-brown and afterwards opaque.—In a concentrated aqueous solution it is converted by *bromine* into terbromo-phloroglucin, which immediately separates in the crystalline form, the liquid becoming hot, and emitting a highly tear-exciting odour. With hot hydrochloric acid it assumes a reddish yellow colour.—*Nitric acid* dissolves it with brown colour, and converts it into nitrophloroglucin (p. 68).—*Ammonia* converts it into phloramine  $C^{12}H^7NO^4$  (p. 69).—It reduces an *alkaline solution of cupric oxide*, like grape-sugar. It reduces *mercurous nitrate* when heated with it, and likewise *nitrate of silver*, with peculiar quickness, on addition of ammonia.—With *chloride of acetyl*, *chloride of benzoyl*, &c., it forms substitution-products (p. 71).

*Combinations: With Water.*—*A. Hydrated Phloroglucin.* Hard crystals belonging to the right prismatic or rhombic system, which by slow evaporation are obtained of the size of peas, with irregular prismatic faces. It grates between the teeth. It effloresces in warm air, and in vacuo, or more quickly at 90°, giving off 22.25 to 22.47 p. c. water of crystallisation (calc. 4 at = 22.22 p. c.), and being thereby converted into anhydrous phloroglucin.

<i>Hydrated.</i>		<i>Hlasiwetz.</i> <i>mean.</i>	
12 C .....	72	44.44	44.45
10 H .....	10	6.18	6.29
10 O .....	80	49.38	49.26
<hr/>		<hr/>	
$C^{12}H^6O^6 + 4Aq$ .....	162	100.00	100.00

*B. Aqueous.*—Phloroglucin dissolves in water, and separates from the solution in the form of hydrate.

It is not altered by cold *hydrochloric acid*. Not precipitated by any *metallic salt*, excepting *basic acetate of lead*. It is coloured deep violet-red by *ferric chloride*, and produces with *solution of chloride of lime*, a reddish yellow colour, which soon disappears.

*Phloroglucin with Potash.*—The solution of phloroglucin in carbonate of potash leaves, when evaporated to dryness, a residue, from which alcohol and ether scarcely take up any phloroglucin, and less, the more nearly they are anhydrous. The alcoholic extract obtained by boiling decomposed phloretin with potash is always turbid, and deposits after some hours, red-brown drops of the compound of phloroglucin with potash (Hlasiwetz, *Wien. Akad. Ber.* 24, 239).

*Phloroglucin with Oxide of Lead.*—Aqueous phloroglucin is precipitated with an insufficient quantity of basic acetate of lead, and the white precipitate is washed several times with water, pressed between paper, then dried in vacuo, and finally at 100°.—It does not turn red on drying.

		<i>Hlasiwetz.</i>	
12 C .....	72	12.41	12.79
6 H .....	6	1.03	1.13
6 O .....	48	8.59	8.48
4 PbO .....	446	77.97	77.60
<hr/>		<hr/>	
$C^{12}H^6O^6, 4PbO$ .....	572	100.00	100.00

Phloroglucin is soluble in *alcohol*, and still more so in *ether*.  
F 2



## Terbromophloroglucin.

HLASIWETZ. *Wien. Akad. Ber.* 17, 394.*Formation.* (p. 67)

*Preparation.* Bromine is dropped into concentrated aqueous-phloroglucin till the colour of the bromine is no longer destroyed, and the liquid has solidified to a crystalline pulp; this product is collected on a filter, washed with cold water, and recrystallised from boiling water with help of animal charcoal.

*Properties.* See Hydrated Terbromophloroglucin. This compound gives off 12.92 p.c. water (calc. 6 at. = 12.94) and then easily falls to powder.

<i>Dried.</i>				Hlasiwetz. <i>mean.</i>
12 C .....	72	...	19.83	20.03
3 Br .....	240	...	66.11	66.07
3 H .....	3	...	0.82	1.37
6 O .....	48	...	13.24	12.53
$C^{12}H^3Br^3O^6$ .....				100.00
363				100.00

Appears to be partly decomposed by boiling with *water*.

*Combinations.* With *Water*.—*A. Hydrated Terbromophloroglucin.* Crystallises from water in long needles (mostly brownish), from alcohol in concentrically united prisms, which give off their water in warm air or at 100°, and are reduced to anhydrous terbromophloroglucin.

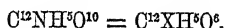
<i>Crystals.</i>				Hlasiwetz. <i>mean.</i>
12 C .....	72	...	17.26	17.44
3 Br .....	240	...	57.31	57.25
9 H .....	9	...	2.15	2.27
12 O .....	96	...	23.28	23.04
$C^{12}H^3Br^3O^6 + 6Aq$ .....				100.00
417				100.00

*B. Aqueous.*—Terbromophloroglucin dissolves very slightly in cold, more freely in boiling *water*.

It is dissolved, with brown colour, by *alkalis* and their *carbonates*.

It dissolves very readily in *alcohol*.

## Nitrophloroglucin.

HLASIWETZ & PFAUNDLER. *Ann. Pharm.* 111, 199.

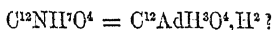
Nitric acid acts violently on phloroglucin, even in the cold, and forms, with great

evolution of heat, a blood-red solution which gives off a large quantity of gas and becomes lighter, oxalic acid being formed in it. When phloroglucin is added by small quantities to somewhat dilute nitric acid moderately heated and kept at a uniform temperature, a deep red solution is formed, which deposits small nodules. These are purified by recrystallisation from hot water.

Reddish yellow shining scales and laminae, having a slightly bitter taste. They are sparingly soluble in water, but colour it yellow.

Hlasiwetz & Pfaundler.					
12 C .....	72	...	42.10	.....	42.04
N .....	14	...	8.18	.....	8.36
5 H .....	5	...	2.92	.....	3.24
10 O .....	80	...	46.80	.....	46.36
<hr/>					
C <sup>12</sup> XH <sup>5</sup> O <sup>5</sup> .....	171	...	100.00	.....	100.00

### Phloramine.



HLASIWETZ & PFAUNDLER. *Wien. Akad. Ber.* 43, 451; *Ann. Pharm.* 119, 202; abstr. *Chem. Centr.* 1861, 610.

Phloroglucin, over which dry ammonia gas is passed, absorbs large quantities of it, and melts; and if, as soon as the formation of water has ceased, the resulting crystalline mass is dissolved in warm water, crystals of phloramine are obtained.—The brown solution of phloroglucin in 5 pts. warm aqueous ammonia, deposits, after standing for some time, crystals which must be purified by recrystallisation from warm water, and dried as quickly as possible in vacuo over oil of vitriol.

*Properties.* Thin, delicate, micaceous laminae, which separate from the filter in the form of a film having a silky lustre. Taste, slightly astringent. Permanent in dry air.

Over oil of vitriol.				Hlasiwetz & Pfaundler.	
				<i>mean.</i>	
12 C .....	72	...	57.60	.....	57.39
N .....	14	...	11.20	.....	11.37
7 H .....	7	...	5.60	.....	5.78
4 O .....	32	...	25.60	.....	25.46
<hr/>					
C <sup>12</sup> NH <sup>7</sup> O <sup>4</sup> .....	125	...	100.00	.....	100.00

*Decompositions.* 1. Phloramine heated over the water-bath acquires a lemon-yellow and ultimately a dirty brown colour, losing weight at the same time and becoming insoluble in water. After 6 hours drying, the loss amounts to 6 p. c.; after 3 hours drying, the product contains 59.82 p. c. C., 5.82 H.; after 4 hours, 60.73 C., 5.77 H.; after 6 hours, 61.38 p. c. C., 5.70 H., and 11.90 N., and therefore differs from phloramine by containing between  $\frac{1}{2}$  and 1 at. less water.—2. Phloramine either moist or dissolved in water turns brown when exposed to the air.—3. *Fuming nitric acid* acts violently on phloramine, producing a yellowish-red solution from which dark brown crystals sepa-

rate, probably a nitro-compound. The same crystals are produced when nitrate of phloramine is kept in the moist state.—4. When phloramine is heated over the water-bath with *oil of vitriol*, a conjugated sulphuric acid is formed, whose baryta-salt crystallises in needles. This baryta-salt and the solution obtained by heating phloramine with oil of vitriol, diluting, neutralising with carbonate of baryta, boiling and filtering, acquires a fine violet colour on addition of sesquichloride of iron, even if the liquid is very dilute, just as tyrosine (xiii. 358) does when similarly treated.—5. By *chlorate of potash* and hydrochloric acid, phloramine is converted into a dark brown resin which gradually becomes lighter in colour, and when distilled, gives off a small quantity of oil having an intensely strong odour (perhaps chlorinated acetone), and leaves a resin. No chloranil is formed in this reaction.—6. When ammoniacal phloroglucin is exposed to the air, the phloramine formed in the first instance disappears, and the liquid dries up to a black shining brittle mass, which dissolves in aqueous ammonia and is thrown down by acids as a black-brown precipitate. This precipitate, after being washed, dried, again washed with warm water, and again dried, resembles pulverised glance-coal, and, though not of perfectly uniform composition, contains, on the average, 59·6 p.c. C., 4·4 H., and 4·2 N. Perhaps, therefore,  $C^{36}NH^{18}O^4$  (calc. 60·5 C., 4·2 H., 3·9 N.), formed from 3 at. phloroglucin, 1 at. ammonia, and 2 at. oxygen, with elimination of 6 at. water.—7. By aqueous *alkalis*, phloramine is coloured dark and decomposed.—8. It does not reduce *silver* from its solution when heated therewith.

*Combinations.* Phloramine is sparingly soluble in cold water. The solution does not colour *sesquichloride of iron*, or form a precipitate with *neutral acetate of lead* or *nitrate of silver*.

It unites with acids, forming *salts* which crystallise well, and are all soluble in alcohol.

*Sulphate of Phloramine.*—A solution of phloramine in dilute sulphuric acid yields by spontaneous evaporation, long, yellowish, brittle needles, which, when heated over the water-bath, acquire a bright yellow colour and give off 9·38 p.c. water (2 at. = 9·37 p.c.)

Dried.		Hlasiwetz & Pfaundler.	
$C^{12}NH^7O^4, HO$ .....	134	...	77·01
$SO^3$ .....	40	...	22·99
$C^{12}NH^7O^4, SO^3, H_2O$ .....	174	...	100·00

Hlasiwetz doubles the formula, in accordance with the bibasicity of sulphuric acid.

*Hydrochlorate of Phloramine.*—Phloramine, on which strong hydrochloric acid is poured, crumbles to a sandy powder, which dissolves when heated, and separates on cooling in yellow shining laminae, perhaps consisting of the anhydrous salt. After solution in water, white needles and laminae are slowly obtained, which turn yellow at 100° and give off 10·16 p.c. water (2 at. = 10·02 p.c.)

Dried.		Hlasiwetz & Pfaundler.	
12 C .....	72·0	...	44·58
N .....	14·0	...	8·67
8 H .....	8·0	...	4·95
4 O .....	32·0	...	19·82
Cl .....	35·5	...	21·98
$C^{12}NH^7O^4, HCl$ .....	161·5	...	100·00

*Nitrate of Phloramine.*—Phloramine dissolves rapidly in warm moderately concentrated nitric acid, the solution yielding the salt in shining bronze-coloured laminae and needles. (Decompositions p. 70.)

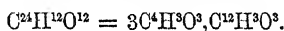
		at 100°		Hlasiwetz & Pfaundler.	
12 C	.....	72	....	38·29	..... 38·23
2 N	.....	28	....	14·89	..... 14·59
8 H	.....	8	....	4·25	..... 4·67
10 O	.....	80	....	42·57	..... 42·51
$C^{12}NH_7O^4, NO^5, HO$		188	....	100·00	..... 100·00

*Acetate of Phloramine.*—The solution of phloramine in glacial acetic acid dries up to a yellow varnish without forming crystals. When water is poured upon it, there remains a yellow powder which when heated partly melts to a resin and partly dissolves.

*Oxalate of Phloramine* crystallises.

Phloramine dissolves readily in *alcohol*, but is insoluble in *ether*.

### Acetyl-phloroglucin.



HLASIWETZ & PFAUNDLER. *Ann Pharm.* 119, 201.

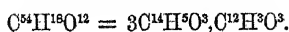
Chloride of acetyl (ix. 191) acts on phloroglucin even at mean temperatures, and at higher temperatures converts it, with evolution of hydrochloric acid, into a white crystalline mass, which, after the excess of chloride of acetyl has been expelled, may be recrystallised from alcohol.

Small colourless prisms which give off acetic acid when heated. Insoluble in water.

		Hlasiwetz & Pfaundler.	
		mean.	
24 C	..... 144	.... 57·14	..... 56·78
12 H	..... 12	.... 4·76	..... 4·97
12 O	..... 96	.... 38·10	..... 38·25
$C^{12}(C^4H^3O^3)^3H^3O^6$		252	.... 100·00 ..... 100·00

So according to the analogy of benzoylphloroglucin.—Analysis gives no means of determining whether 1, 2, or 3 at. acetyl have entered into the phloroglucin in place of hydrogen, inasmuch as all three products would have the same percentage composition. (Hlasiwetz).

### Benzoyl-phloroglucin.



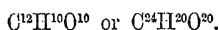
HLASIWETZ & PFAUNDLER. *Ann. Pharm.* 119, 201.

Produced by the action of chloride of benzoyl on phloroglucin, and purified by boiling with alcohol, in which it is nearly insoluble. Small, white, shining scales.

				Hlasiwetz & Pfaundler.			
54 C	.....	324	....	73.97	.....	73.59	
18 H	.....	18	....	4.11	.....	4.31	
12 O	.....	96	....	22.02	.....	22.10	
$C^{12}(C^{14}H^5O^2)^3H^3O^6$				438	....	100.00	..... 100.00

*Carbo-hydrates*  $C^{12}H^{10}O^{10}$ .

## Starch.



- KIRCHHOFF. (1811.) *Schw.* 4, 112.—14, 388; *Scher. N. Bl.* 1, 144.  
 SCHERER. *Scher. N. Bl.* 1, 134.  
 GEHLEN. *Schw.* 5, 32.  
 VOGEL. *Schw.* 5, 80; *Gillb.* 42, 123.—*Gillb.* 64, 167.  
 BERZELIUS. *Ann. Chim.* 95, 82.—*Ann. Pharm.* 30, 89; *J. pr. Chem.* 17, 180; *Compt. rend.* 1839, 528; *Ann. Chim. Phys.* 70, 215.  
 DANIELL. *Ann. Chim. Phys.* 10, 219.  
 TH. DE SAUSSURE. *Ann. Chim. Phys.* 2, 387.—11, 379; *Schw.* 27, 301; *N. Tr.* 4, 2, 112.—*Bibl. univers.* 53, 260; abstr. *J. Pharm.* 19, 578; *Schw.* 67, 188; *Pogg.* 32, 194.  
 COUVERCHEL. *J. Pharm.* 7, 267.  
 CAVENTOU. *Ann. Chim. Phys.* 31, 337; *N. Tr.* 13, 2, 89.  
 RASPAIL. *Ann. Sc. nat.* 2.—*Ann. des Sc. d'observation* 3, 216.  
 DUBRUNFAUT. *Mém. de la Soc. centr. d'agricult.* 1823, 146.  
 GUIBOUT. *J. Chim. méd.* 5, 96; *Br. Arch.* 31, 276; abstr. *Ann. Chim. Phys.* 40, 183; *Schw.* 56, 78; *N. Tr.* 19, 2, 93.  
 PAYEN. *J. Chim. méd.* 2, 237.—9, 507 & 569; *Ann. Chim. Phys.* 53, 82; abstr. *Schw.* 69, 119.—*Inst.* 103, 135; abstr. *Pogg.* 37, 154.—*Compt. rend.* 14, 533; *Ann. Pharm.* 30, 95; *J. pr. Chem.* 17, 185.—*Comp. rend.* 18, 240.—23, 337.—25, 147.—48, 67; abstr. *Chim. pure* 1, 233; *N. J. Pharm.* 35, 106; *Inst.* 1859, 20.—*Ann. Chim. Phys.* 61, 355.—*N. Ann. Sc. nat. Bot.* 10, 58, 65, 8, 161; *Ann. Chim. Phys.* 65, 225; abstr. *J. pr. Chem.* 14, 65.  
 PAYEN & PERSOZ. *J. Chim. méd.* 9, 582.—*Ann. Chim. Phys.* 56, 337; *J. pr. Chem.* 4, 288; abstr. *Pogg.* 37, 128.  
 CHEVREUL. *Inst.* 62, 256; abstr. *Pogg.* 32, 398.  
 DUMAS. *Inst.* 10, 82; abstr. *Pogg.* 37, 174.—*Traité de Chimie appliquée aux arts*, 6, 81.—*Ann. des Sc. natur.* 1839.  
 BIOT & PERSOZ. *Ann. Chim. Phys.* 52, 72; *Schw.* 68, 163; abstr. *Pogg.* 32, 160; *Ann. Pharm.* 6, 209.  
 GUÉRIN-VARRY. *Ann. Chim. Phys.* 56, 225; *J. pr. Chem.* 3, 329; abstr. *Ann. Pharm.* 13, 71; *Pogg.* 37, 118.—*Ann. Chim. Phys.* 57, 108.—*Ann. Chim. Phys.* 60, 32: abstr. *Ann. Pharm.* 17, 26; *Pogg.* 37, 141.—*Ann. Chim. Phys.* 61, 66; *J. pr. Chem.* 7, 205.  
 FRITZCHE. *Pogg.* 32, 128.  
 MULDER. *J. pr. Chem.* 15, 299.  
 BRUNNER. *Pogg.* 34, 319.  
 POGGENDORFF. *Pogg.* 37, 114.  
 JACQUELAIN. *Ann. Chim. Phys.* 73, 167.  
 MITSCHERLICH. *Pogg.* 55, 221; *N. Ann. Chim. Phys.* 7, 27.

- BIOT. *N. Ann. Chim. Phys.* 11, 100; *Inst.* 3, 13.  
 BLONDEAU DE CAROLLES. *Rev. Scient.* 15, 69; abstr. *J. pr. Chem.* 33, 439; *Ann. Pharm.* 52, 416.  
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 FEHLING. *Ann. Pharm.* 55, 13.  
 SCHWARZ. *Ann. Pharm.* 70, 55.  
 BALLING. *Gährungschemie, Prag.* 1845, 2, 11.  
 SCHLEIDEN. *Grundzüge der wissenschaft. Bot.* Leipzig, 1849, 1, 176.  
 J. DEAN. *Value of different kinds of prepared vegetable food.* Cambridge, U.S., 1854.  
 BÉCHAMP. *Compt. rend.* 39, 653; *Inst.* 1854, 338; *J. pr. Chem.* 64, 38; *Pharm. Centrbl.* 1854, 863.—*Compt. rend.* 42, 1210; *N. Ann. Chim. Phys.* 48, 458; abstr. *Inst.* 1856, 234; *Ann. Pharm.* 100, 364; *J. pr. Chem.* 69, 447.  
 NÄGELI. *Flora*, 1856, No. 38 — 41; abstr. *Pharm. Vierteljahr.* 6, 256.—*Die Stärkmehlkörner*, 1858.  
 TRÉCUL. *Compt. rend.* 47, 685 & 782; *Inst.* 1858, 358.  
 NIEPCE & CORVISART. *Compt. rend.* 49, 368; *Inst.* 1859, 287; abstr. *Ann. Pharm.* 113, 112.

*Memoirs especially relating to Iodide of Starch.*

- COLIN & GAULTIER DE CLAUERY. *Ann. Chim.* 90, 93; *Schw.* 13, 453; *Gilb.* 48, 298.  
 STROMEYER. *Gilb.* 49, 146.  
 BRUGNATELLI. *Ann. Chim. Phys.* 4, 384.  
 GIESECKE. *Schw.* 43, 367.  
 PAYEN. *J. Chim. méd.* 8, 513.—9, 449; *Ann. Chim. Phys.* 53, 109; *Pogg.* 39, 624; *Schw.* 69, 85.—*J. Chim. méd.* 9, 648 & 705.—14, 269.  
 LANGLOIS. *J. Pharm.* 20, 576.  
 JACQUELAIN. *Ann. Chim. Phys.* 73, 196.  
 PELLETIER. *Bull. Pharm.* 6, 288.  
 BLONDLOT. *N. Ann. Chim. Phys.* 43, 225; *N. J. Pharm.* 28, 45.  
 BÉCHAMP. *N. J. Pharm.* 27, 406.—28, 303.  
 PISANI. *Compt. rend.* 43, 1118; *J. pr. Chem.* 70, 382.

*Memoirs relating especially to soluble starch.*

- MASCHKE. *J. pr. Chem.* 56, 409; *Pharm. Centrbl.* 1852, 609; *J. pr. Chem.* 61, 1; *Pharm. Centrbl.* 1854, 337; *N. J. Pharm.* 25, 237.  
 BÉCHAMP. See above.

*Stärke, Satzmehl, Kraftmehl, Amylum, Amidon, Matière amylacée.*—Known to the ancients; prepared from wheat, especially in Crete and in Egypt; according to Dioscorides, it was called *ἀμύλον* by the Greeks, because it could be obtained without grinding with mill-stones. It was first separated from flour by Beccari, in 1745.

*Sources.* Starch is very widely diffused in the vegetable kingdom. It occurs in variable quantity, for a time, at least, in every plant that has been examined. It is especially abundant in certain families of plants, and occurs in very large quantity in certain organs, especially in the albumen of the seeds (not in those of acotyledons: Wahlenberg *N. Gehl.* 81, 108), in the cotyledons of the embryo; in the pith of the stem and stalks; in bulbs, tubers, rhizomes, and roots; also in the bark and splint of trees in the winter-season; sometimes in the flowers. It

is enclosed in vegetable cells, which it often fills completely, or is scattered therein in granules, but is never attached to the cell-walls (Payen *Compt. rend.* 18, 240); according to Turpin, on the contrary, the starch granules are attached by their *hilum* to the wall of the cell. Starch may occur in the cells of all organs of the greater number of plants, but not in the youngest cellular tissue, which is composed of nitrogenous matter and cellulose; thus, it does not occur in the spongioles of the roots, the youngest leaf-buds, or the youngest forms of the flower, in the interior of the unimpregnated ovary, in the epidermis and cells lying immediately under it, or in the vessels and intercellular passages. (Payen.)

Woody plants, which are green in summer, contain in spring, before the commencement of vegetation, granular starch, which, as the sap begins to move, is gradually dissolved from without, inwards. It is distributed through all parts of the stem, both above and below the surface of the ground, in the cells of the parenchyma and prosenchyma, being most abundant in the underground wood, less in the stem-wood, least in the branch and twig-wood; but in *Fagus Sylvatica* and *Carpinus betulus*, it is most abundant in the cells of the medullary rays of the youngest shoots. (Hartig, *J. pr. Chem.* 5, 217; see also, Waldenberg, *N. Gehl.* 8, 108; Robert, *J. Pharm.* 4, 545; Hüncfeld, *J. Pharm.* 16, 664.)

Starch has been found and partially examined in the following plants, among others: in some *Conferve* (Mohl, Meyer); in some *Charæ*, but not in all; in the stalks of *Lycopodiaceæ* (not in the seeds: Schleiden), in the cellular tissue of the stem and branches of some *Rhizocarpeæ*; in the leaf-buds of *Marchantia* and *Lamularia* (Vogel, *Linnaea*, 15, 59; *J. pr. Chem.* 25, 382).—In the roots of *Arctium Lappa*, *Atropa Belladonna*, *Polygonum Bistorta*, *Spiræa filipendula*, *Scrophularia nodosa*, *Sambucus Ebulus*, and *S. nigra*, *Imperatoria Ostruthium*, *Bunium Bulbocastanum*, *Orobis tuberosus*, several species of *Rumex*, *Hyoscyamus niger* (Parmentier); *Convolvulus Jalappa* and *C. Turpetum*, *Rheum palmatum*, and *R. rhaponticum*, *Pæonia officinalis*, *Valeriana officinalis*, *Aristolochia Clematitis*, and *A. Serpentaria*, *Polypodium Filix mas*, *Geum urbanum*, *Alpinia Galanga*, *Fragaria vesca*, *Nymphaea alba*, *Brassica Napus*, *Laurus Sassafras*, *Apium Petroselinum*, *Urtica dioica*, *Daucus Carota* [according to C. Schmidt (*Ann. Pharm.* 83, 326), it is not found in this plant, but according to Wittstein (*Pharm. Vierteljahr.* 2, 122) it is], *Tropæolum majus* (not in the roots, but in the stem, leaf-stalks and seeds; Hüncfeld), in various species of *Rumex*, *Malva sylvestris*, *Glycyrrhiza glabra*, *Cochlearia armoracia* (not in the seeds, Hüncfeld). *Athura officinalis*, *Ononis spinosa*, *Humulus Lupulus* (Robert, *J. Pharm.* 4, 542); of *Aselepias syriaca* (not in the part of the plant growing above ground), abundantly in the roots of *Triglochin maritimum*, of various species of *Plantago*, in *Orchidaceæ*, *Iridaceæ*, *Ranunculaceæ*; sparingly in the several species of *Rumex*, not at all in the roots of *Syngenesiæ* and *Tetradynamici* (Hüncfeld); of *Cephalis Ipecacuanha* (Willigk, *Wien. Akad. Ber.* 5, 190), *Bryonia alba* (Parmentier, Riegel, *Jahrb. pr. Pharm.* 6, 35), *Cocculus palmatus*, *Pastinaca sativa* (Payen); of various species of *Arum*, *Callodium Succulentum*, various species of *Jatropha* (Ricord, Madianna, *J. Pharm.* 16, 313; *Schw.* 59, 247); of *Smilax Sarsaparilla*, *Daucus Carota* (Schleiden.) In the tubers of *Solanum tuberosum*, of *Orchidaceæ*, of *Aponogeton* (Payen) of *Ipomœa Batatas* and *I. operculata* (Buchner, *Repert.* 31, 393), *Oxalis crenata* (Payen).—In the root-stocks of *Muranta arundinacea* and *M. indica*, of various species of *Canna* (Payen, Fritzsche, Schleiden,

Ricord, Madianna); *Zea Mais* (Payen, Schleiden); *Zinziberaceæ* and *Dioscoreæ* (Ricord, Madianna, Schleiden); *Hedychium* (Fritzsche); *Veratrum album*, *Acorus Calamus*, *Iris germanica* (Robert); *Curcuma angustifolia* (Guibourt); *Curcuma leucomrhiza*, *Carex arenaria*, *Anatherum lamarumense*, *Iridaceæ*, *Lathræa squamaria* (Schleiden).—In the nodular roots of *Ficaria verna* (Schleiden).—In the bulbs of *Liliaceæ* and *Colchiaceæ* (Schleiden).—In the stalk of *Bernhardia dichotoma* (Schleiden); in the wood-stem of *Aesculus Hippocastanum*, *Carpinus Betulus*, and various species of *Populus*, *Salix* and *Tilia*, amounting to between 5 and 26 per cent. of the wood (Hartig, *vid. sup.*); in the wood-stem of *Cycadææ* and species of *Sagus* (Payen, Guibourt, Schleiden), *Cactaceæ* (Payen), *Bleelia Tankervilleæ*, *Dieffenbachia seguine* (Schleiden), *Aruno saccharifera*, *Phoenix faranifera* (Guibourt).—In the bark of *Aglanthus glandulosa* (Schleiden), sparingly in the bark of *Pinus sylvestris*, *Populus nigra*, *Laurus Massoy*, *Geoffroya surinamensis* and *G. Jamaicensis*, *Drinys Winteri* (Hünefeld).—In the thickened parenchyma of the leaves of *Marullia* (Schleiden).—In the green parts of *Chenopodium ambrosioides*, *Achillea millefolium*, *Galeopsis officinalis*, *Teucrium marum*, *Atropa Belladonna*, *Calendula officinalis* (Hünefeld).—In the flowers (not in white flowers) of *Tropæolum majus*, *Helianthus annuus*, *Oenothera grandiflora*, *Potentilla punica*, *Heliopsis*, *Tagetes erecta*. (Hünefeld, *J. pr. Chem.* 16, 87).—In unripe apples and pears Döbereiner, *J. pr. Chem.* 28, 167; Payen, *Compt. rend.* 53, 813). The existence of starch in unripe fruits has been denied by some authors; but, according to Payen, it may always be found in unripe fruits having an acid juice, if the following method of observation be adopted: A thin, vertical slice of the fruit is cut, and immediately plunged into water, in order to avoid the action of the air on the colouring matter contained in it, and to remove from its surface all those soluble substances which might absorb iodine. After this washing, an aqueous solution of iodine, slightly alcoholised, is substituted for the water, and the slices are left under the influence of this solution for an hour or two. Apples, pears and quinces, which have attained to a quarter or half their development, exhibit, when thus treated, the blue or deep violet colour which indicates the presence of starch. In the seeds of *Graminaceæ* (in the cereals, however, only for a short time before and during maturity; Hünefeld), of *Leguminosæ*, *Chenopodiaceæ*, *Amaranthaceæ*, *Caryophyllaceæ*, *Portulacæ* (Trécul), of *Beta vulgaris* (Payen), *Momea americana*, *Laurus*, *Melia sempervirens* (Ricord), *Zea Mais*, *Oryza sativa* (Payen, Lassaigue, *J. Chim. méd.* 22, 4), *Alpinaria Cardamomum* (Schleiden), *Castanea vesca* (*Bianche di Como*, 37.5 p. c.; *B. di Orta*, 38.02; *Val Travaglia*, 23.0; *Vallellina*, 23.3 p. c.), (Albini, *Wien. Akad. Ber.* 13, 502). *Aesculus Hippocastanum* (Flandin, Belloc). *Theobroma Cacao* (Lampadius, Buchner, *Repert.* 58, 166); not in the seed of *Theobroma Cacao* (Delcher & Chevallier, *J. Chim. méd.* 14, 467; Herzog, *N. Br. Arch.* 96, 216), in some varieties (Bloy, *loc. cit.*). In *Trehala*, the exudate of a species of *Echinops*, probably a native of Syria, to the amount of 66.54 per cent., together with trehalose and gum. (Guibourt, *Compt. rend.* 46, 1213.)

Starch is formed in plants only when the nutriment is in excess, and is dissolved and used up at a later stage of the vegetative process, when the nutriment becomes deficient (Payen): it is probably formed from vegetable mucus (Schleiden). Before the starch appears in the cells, they are filled with a granular or homogenous mass (*protoplasma*), the development of which is slower than that of the cell, so that it spreads itself in a layer of varying thickness over the inner surface of the cell, enveloping the nucleus perhaps already present, and sometimes



spreading in a thread-like form over its surface; the starch is most frequently formed in this protoplasm, more rarely on the surface or in the interior of the nucleus. (Trécul, *Compt. rend.* 47, 782.)

On the quantity of starch in different parts of plants, according to Krockner (*Ann. Pharm.* 58, 212), see in *Gmelin's Handbuch*, Band VIII, *Phytochemie*, s. 672; also *Gerhardt's Traité*, tom. ii. p. 486.

2. *In the Animal Kingdom.* In the spleen, liver, kidneys, mucous membrane, bladder, and brain, in variable quantities, sometimes in the mucus of the bronchiæ and bladder, in the urine, in cancerous and tuberculous exsudations (Carter, *N. Ann. Chim. Phys.* 56, 358; *Rép. Chim. pure*, 1, 475).—A substance resembling starch is found in the epithelial cells of the membranes of the amnios and placenta; in the epidermal cells of the skin, gums, and tongue; in the epithelium of the stomach and intestines (Rouget, *Compt. rend.* 48, 792; *Rép. Chim. pure*, 1, 395). According to Dobson, it occurs in the secretion of the *Psylla*, an insect which lives on the leaves of the *Eucalyptus* (Trécul, *Compt. rend.* 47, 688).

On *animal amyloid*, a substance nearly resembling starch, see *Handbuch* Band VIII, *Zoochemie*, s. 75; the recent observations of Kekulé and Paulitzky (*Schmidt's medic. Jahrb.* 103, 7 and 10); on the (not yet isolated) vegetable amyloid, see Vogel & Schleiden. (*Pogg.* 46, 327).—The hordein or cevadin found by Proust (*Ann. Chim. Phys.* 5, 339) and Bizio, in the grain of barley and in maize, is, according to Braconnot (*Ann. Chim. Phys.* 35, 159) and Guibourt (*J. Chim. méd.* 5, 158; *Schw.* 56, 119), a mixture of woody fibre, starch, and nitrogenous matter.

*Preparation.* 1. *From Wheat.*—Wheat-starch, *Weizenstärkemehl*, *Weizenstärke*, *Amidam*, *Amidone*.—Wheat after being softened in cold water, is pressed under mill-stones or rollers, or in bags under water, as long as milky water runs off from it. This liquid, when left to itself, deposits starch containing gluten; the latter, however, dissolves for the most part in the supernatant liquid, which gradually turns sour (sour water), and on decanting this acid liquid, repeatedly stirring up the starch with fresh water, and leaving it to settle, it is at length obtained pure, and may be dried in suitable desiccating chambers.—Wheat-flour is mixed with 4 to 5 volumes of water, and  $\frac{1}{3}$  to  $\frac{1}{10}$  vol. sour water obtained from former operations; this sets up a fermentation, which lasts from 2 to 4 weeks, according to the temperature, and is interrupted as soon as the nitrogenised substances are decomposed and dissolved. The sediment of starch which remains at the end of a fermentation, is repeatedly washed with water, sifted, and dried in desiccating chambers.—Starch may be freed from gluten by means of cold, dilute potash-ley (Kirchhoff), or by distilled vinegar (Saussure), from pieces of fat and other matter, by prolonged treatment with cold water, alcohol, or ether.

2. *From Potatoes.*—Potato-starch, *Kartoffelstärkemehl*, *Fécule*.—Washed and rasped potatoes are drenched in a sieve with a continued stream of cold water, and the milky liquid which runs through is set aside for a few minutes, till the heavier impurities have settled down, and then left to stand for 3 or 4 hours in another pan. The starch which collects at the bottom of the clear liquid is stirred up with water, poured through hair sieves, then left to settle, repeatedly washed with cold water, and dried, first on plates of gypsum, afterwards in desiccating chambers. The starch thus obtained is purified by successive

washing with the following liquids:—1. Cold alcohol.—2. Water.—3. Water containing 0·002 p. c. hydrochloric acid.—4. Water.—5. Water containing 0·005 p. c. potash.—6. Water. (Payen). After this treatment, the starch contains hydrochloric acid (Jacquelin, Gerhardt *Traité*, 2, 486), but may be purified by boiling with alcohol containing 0·1 p. c. hydrate of potash, then washing with pure alcohol and with water.

3. *From the root-sprouts of Maranta indica and M. arundinacea.*—American starch, Arrow-root.—Mode of preparation the same as 2.

4. *From the roots of Janipha Manihot.*—Tapioca.—The washed and bruised roots are pressed in bags under water; the starch which separates from the milky liquid is *mealy tapioca*; after drying upon hot plates, it becomes *granular tapioca*; the portion of the pulp which remains after washing and pressing is spread out on iron plates in a layer 1 or 2 inches deep, and strongly dried into cakes; this is *Cassava bread*; when pulverised it forms *Manjok flour*, and when again heated on iron plates till it swells up; *Mandiokka*. (Sureau, *J. Pharm.* 20, 622).

5. *From the stems of several species of Sagus and Cycas.*—Sago.—The starch is washed out of the pith of the stems on sieves in a stream of water, then left to settle, washed on cloths or mats, rubbed when half dry through metal sieves, and when thus granulated, it is dried at about 60° in ovens of peculiar construction.

6. *From Rice.*—Rice is heated with weak soda-ley, which dissolves the nitrogenous impurities, and leaves pure starch (Lassaigne, *J. Chim. méd.* 22, 4), then with a solution of borax, cream of tartar, or some other salts, to facilitate the separation of the starch from gluten. (Colmann, *Rep. of pat. inventions*, 38, 178.)

7. *From Horse-chestnuts, &c.*—The same method as in 2, excepting that the starch is likewise well washed with aqueous carbonate of soda, to remove the bitter principle (Flandin, *Compt. rend.* 27, 349), or merely with water, like potato-starch (Belloc, *Compt. rend.* 28, 83).

*Properties.* White shining powder, soft to the touch, grating between the fingers or the teeth, sometimes consisting of amorphous masses, but more frequently of granules recognisable by the microscope.—These granules, of various diameter (from  $\frac{3}{16}$  to  $\frac{1}{1000}$  of a line, Fritzsche), (from ·185 to ·002 millimetres, Payen), and form (Payen), (mostly egg-shaped, according to Fritzsche & Schleiden), have generally a small eccentric nucleus (Fritzsche's *nucleus*; Schleiden's *central cavity*), surrounded by layers arranged concentrically one over the other (Fritzsche, Payen, Schleiden). These envelopes increase by the successive deposition of new layers within the old ones (Schleiden), so that each layer is younger and less compactly aggregated than the one which immediately surrounds it (Payen); and since the layers are for the most part of variable thickness, they cause the granule to deviate gradually in form from the originally spherical nucleus. (Schleiden.)—According to Maschke, the starch-granules appear like bundles of 3—6 concentric bladders, with light and dark rings, the light rings being formed of insoluble, the dark of soluble, starch, and enclosing the central cavity of the innermost bladder, which is either empty or filled with liquid amylose. According to Pohl

(*J. pr. Chem.* 83, 35), the stratification of starch-granules is perceptible only when they are immersed in water [possibly because the dry starch is not sufficiently transparent].

1. *Amorphous Starch*, in the albumen of *Cardamomum*, in Jamaica sarsaparilla root, in the root-stock of *Carex arenaria* (Schleiden); dissolved in the epidermal cells of *Gagea lutea* and several species of *Ornithogalum* (Sano & Schumck); only partially granular in the root of *Aristolochia*. (Trécul.)

2. *Simple starch-granules*. — *a. Roundish*. With apparently deficient nucleus: throughout the vegetable kingdom; with small round nucleus and distinct lamination: very crude in the pith of *Cycadaceæ*; egg-shaped in potatoes, in the root-stock of *Maranta*, *Canna*, &c.; conchoidal in the larger *Liliaceæ*; with indistinct or deficient lamination, rounded and many-angled, in maize; sharp-edged, with numerous summits, in rice; with elongated nucleus, roundish or egg-shaped, and exhibiting a star-shaped crack in the inner layers when dry, in *Leguminosæ*; hollow, apparently cup-shaped, in the root-stock of *Iris florentina* and allied species. — *b. Flattened lenticular*. With or without lamination, the nucleus being central or eccentric, sometimes roundish or elongated, or with a star-shaped fissure, in the cereals. — *c. Flat dish-shaped*. With distinct lamination: in *Zinziberaceæ*. — *d. Bar-shaped*. With elongated nucleus: in the milky juice of European and of some tropical *Euphorbiaceæ*. — *e. Quite irregular*: in the milky juice of many tropical *Euphorbiaceæ*. (Schleiden.)

3. *Composite granules*. — *a. The individual granules having no distinct nucleus*. United by twos, threes, and fours, in the simplest manner: in the *Marantaceæ* (Arrow-root), in *Marattea*, and in the root of *Bryonia*; — united, for the most part regularly, in groups of 2 — 6: in the root-bark of *Sarsaparilla*. — *b. The individual granules in the groups having a distinct nucleus*. United in groups of 2 — 4, cells of uniform size, with small roundish nucleus: in the root of *Janipha Manihot*; with large nucleus, split in beautiful stellate form: in *Colchicum* bulbs; composed of 2 — 4 apparently cup-shaped nuclei: in the root of *Anatherum Ivarancusa*; of 2 — 12 granules in irregular groups: in the tubers of *Arum Maculatum*. — *c. Small granules grouped round a large grain*: in the several kinds of sago. (Schleiden.)

On the structure of starch-grains in arrow-root, *Dioscorea alata*, *Helianthus tuberosus*, batatas, potato and *Orchidaceæ*, see Payen (*J. Chim. méd.* 2, 237); in wheat, arrow-root *Jatropha*, sago, and *Orchidaceæ* (Guibourt, *J. Chim. méd.* 5, 96); in *Bryonia* (Riegel, *Jahrb. Pharm.* 6, 35), in rice (Lassaigne, *J. Chim. méd.* 22, 4), in *Anemone nemorosa* and *Arum maculatum* (Enz, *Pharm. Vierteljah.* 5, 97); in various plants (Soubeiran, *N. J. Pharm.* 25, 89, and 175; Field, *Pharm. J. Trans.* 14, 253; Grundy, *Pharm. J. Trans.* 14, 446; Nägeli *Ueber die Structure der Stärkmehlkörner*, 1858); in the *Trehala* (Guibourt, *Compt. rend.* 46, 1215). — On the structure of starch-granules in the spleen and liver, see Carter, *N. Ann. Chim. Phys.* 56, 368; *Rép. Chim. pure*, 1 475. — On the appearances exhibited by the starch-granule when examined by the microscope in polarised light by means of a double refracting prism, see Biot, *Compt. rend.* 5, 905; 13, 795. — *N. Ann. Chim. Phys.* 11, 100).

The following table exhibits the greatest diameter of several kinds of starch-granules, according to Payen (*N. Ann. Sc. nat. Botan.* 10, 65):

Starch from—	Millimetre.
Large Rohan potatoes .. .. .	0·185
<i>Menispermum palmatum</i> (colombo-root) .. .. .	·180
Rhizomes of <i>Canna gigantea</i> .. .. .	·175
Rhizomes of <i>Canna discolor</i> .. .. .	·150
„ „ <i>Maranta arundinacea</i> (arrow-root) .. .. .	·140
Various kinds of potatoes .. .. .	·140
Bulbs of the lily .. .. .	·115
Tubers of <i>Oxalis crenata</i> .. .. .	·100
Stem of a very large <i>Echinocactus erinaceus</i> (imported) .. .. .	·075
Sago .. .. .	·070
Broad beans .. .. .	·075
Lentils .. .. .	·067
Haricot beans .. .. .	·063
Peas .. .. .	·050
Grain of White Wheat .. .. .	·050
Fresh pith of sago-tree ( <i>Cycadaceae</i> ) .. .. .	·045
Hyacinth-bulbs .. .. .	·045
Tubers of Spanish potato ( <i>Batatas edulis</i> ) .. .. .	·045
Corns of <i>Orchis latifolia</i> and <i>bifolia</i> .. .. .	·045
Maize (white, yellow, and violet) .. .. .	·030
Fruit of Chinese sugar-cane ( <i>Sorghum saccharatum</i> ) .. .. .	·030
Stem of <i>Cactus peruvianus</i> .. .. .	·030
Seeds of <i>Naias major</i> .. .. .	·030
Stem of <i>Cactus pereskia grandiflora</i> .. .. .	·0225
Seeds of <i>Aponogeton distachyum</i> .. .. .	·0225
Stem of <i>Ginkgo biloba</i> ( <i>Salisburia adianthifolia</i> ) .. .. .	·022
„ <i>Cactus brasiliensis</i> .. .. .	·020
Fruit of <i>Panicum italicum</i> .. .. .	·016
Half-grown seeds of <i>Naias major</i> .. .. .	·016
Pollen of <i>Globba nutans</i> .. .. .	·015
Stem of <i>Cactus flagelliformis</i> .. .. .	·015
„ <i>Echinocactus erinaceus</i> (grown in hothouse) .. .. .	·012
Pollen of <i>Rupia maritima</i> .. .. .	·011
Stem of <i>Opuntia tuna</i> and <i>Ficus indica</i> .. .. .	·010
„ <i>Opuntia curassavica</i> .. .. .	·010
Fruit of <i>Panicum miliaceum</i> (millet) .. .. .	·010
Stem of <i>Cactus mammillaria discolor</i> .. .. .	·008
Bark of <i>Aylenthus glandulosa</i> .. .. .	·008
Stem of <i>Cactus serpentinus</i> .. .. .	·0075
Parsneps .. .. .	·0075
Pollen of <i>Naias major</i> .. .. .	·0075
Stem of <i>Cactus monstuosus</i> .. .. .	·006
Seeds of beet-root .. .. .	·004
„ <i>Chenopodium Quinoa</i> .. .. .	·002

The specific gravity of starch is 1·505 at 19·7°. (Payen.)—The variations in its specific gravity are due to varieties in the structure of the starch-granules. (Payen & Chevalier, *J. Pharm.* 9, 187.)—It has neither taste nor smell. Potato-starch, not arrow-root starch (Pohl, *J. pr. Chem.* 83, 40), has a peculiar smell, caused by its containing a certain quantity of a volatile oil (Payen, *Compt. rend.* 23, 489).—Neutral. (Guérin-Varry.) (Potato-starch turns vegetable reds blue: Payen).

*Potato-starch.*

				Guérin-Varry. at 100°.	Berzelius. at 100°.	Mulder. at 100°.
24 C	144	...	44.44	43.64	44.25	43.86
20 H	20	...	6.17	6.26	6.67	6.28
20 O	160	...	49.39	50.10	49.08	49.86
<hr/>						
$C^{24}H^{20}O^{20}$	324	...	100.00	100.00	100.00	100.00
				Brunner. in vacuo.	Payen. at 100°.	Jacquelin. at 140°.
C	44.10	...	40.05	43.18	45.03	44.17
H	6.47	...	6.53	6.10	6.37	6.37
O	49.43	...	53.42	50.72	48.60	49.46
<hr/>						
...	100.00	...	100.00	10.000	100.00	100.00

*Wheat-starch.*

			Prout.		Fr. Marcet.	Dean.
			at 100°.	air-dried.	at 100°.	at 160°.
C	43.55	...	37.50	42.80	44.00	43.70
H	6.77	...	6.94	6.35	6.20	6.70
O	49.68	...	55.56	50.85	49.80	49.60
<hr/>						
100.00	...	100.00	...	100.00	...	100.00

*Arrow-root.*

			Prout.	Payen.			Dean.
			air-dried.	at 100°.	at 80°.	at 100°.	at 140°.
C	36.40	...	44.40	42.89	43.69	43.06	43.35
H	7.07	...	6.18	6.35	6.25	6.10	6.40
O	56.53	...	49.42	50.76	50.06	49.94	50.25
<hr/>							
100.00	...	100.00	...	100.00	...	100.00	100.00

*Maize.**Tapioca.**Sago.**Bean-starch.*

		Maize. Dean. at 100°.	Tapioca. Dean. at 100°.	Sago. Dean. at 100°.	Bean-starch. Payen. at 80°.
C	43.73	...	43.70	43.58	42.55
H	6.59	...	6.49	6.31	6.12
O	49.68	...	49.81	50.11	51.33
<hr/>					
100.00	...	100.00	...	100.00	100.00

*Bean-starch.**Parsnep-starch.*

		Payen. at 100°.	Payen.		
			at 80°.	in vacuo.	at 100°.
C	43.76	...	42.93	44.34	43.80
H	6.00	...	6.50	6.30	6.39
O	50.24	...	50.57	49.36	49.81
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100.00	...	100.00	...	100.00	100.00

Early formulæ for starch:  $C^{14}H^{13}O^{12}$ , Berzelius;  $C^{20}H^{17}O^{17}$ , Prout;  $C^{17}H^{10}O^{10}$ , Guérin-Varry; more recent formulæ:  $C^{12}H^{10}O^{10}$ , Mulder;  $C^{12}H^{10}O^9HO$ , Payen.—The opinion which was expressed by Leeuwenhoek, as early as 1716, as to the difference between the envelope of starch-granules and the substance contained within it, was confirmed by Raspail (*N. Syst. de Chim. org.* 1833), who, however, considered the contents as chemically different from the envelope of the starch-granules, and as identical with gum arabic; Guibourt (*J. Chim. méd.* 5, 96) regarded both envelope and contents as chemically the same and only differing in their state of aggregation; he named the contents of the granules, which Raspail had called gum, *fécule soluble*, and supposed it to be identical with the substance, called *Amidin* by Saussure (*Ann. Chim. Phys.* 11, 385) and *Amidon modifié* by Caventou (*Ann. Chim. Phys.* 31, 337), which is formed, according to the latter, when starch is boiled with water, or heated above  $100^{\circ}$  without water. Guérin-Varry nevertheless concluded, from the behaviour of starch with water, that it must contain three constituents, and called the portion soluble in cold water *Amidine*, that which is insoluble in boiling water (the envelope) *Amidine tégumentaire*, and that which by itself is insoluble in cold water, but is rendered soluble by the amidine, *Amidine soluble*. According to him, starch consists of 2.96 p.c. *amidine tégumentaire*, 38.38 *amidine soluble*, and 58.68 *amidine*; the composition of *amidine tégumentaire* and of *amidine soluble* corresponds to the formula  $C^7H^5O^4$ , that of *amidine* to the formula  $C^{10}H^5O^6$ , and hence the composition of starch (*Amidone*), which consists of *amidine* and *amidine soluble*, must be represented by the formula  $C^{17}H^{10}O^{10} = C^{10}H^5O^6 + C^7H^5O^4$ .—Payen & Persoz (*Ann. Chim. Phys.* 56, 337) regard starch (*Amidone*), excepting the envelope of the granules, amounting to 0.4—0.5 per cent., as a single substance, and Guérin-Varry's *amidine* as partially decomposed amidone, his *amidine soluble* as amidone in the free state, and his *amidine tégumentaire* as *amidine* with the envelopes of the granules. Payen (*N. Ann. Sc. nat. Bot.* 10, 201) recognises no chemical difference between the envelope and contents of starch-granules, and ascribes the different behaviour of the outer and inner layers to certain solvents, to the former containing a certain quantity of albumin, fixed and volatile oil, lime-salts, and other matters. Wheat-starch contains, according to Rousseau (*Pogg.* 32, 101), 0.005—0.006 per cent., and potato-starch 0.001 per cent. of a white tallow, easily soluble in alcohol; according to Guérin-Varry, nothing but chlorophyll and wax, and no volatile oil (Potato-fusel-oil), whose existence ready formed in the envelopes of the granules was assumed by Payen (*Ann. Chim. Phys.* 53, 82; *J. Chim. méd.* 9, 507). Comp. Dubrunfaut & Beudant.—According to Blondeau de Carolles, all the layers of the starch-granule are chemically the same, but differ in density. According to Melsens (*Inst.* 1857, 161), starch probably consists of a nitrogenous substance (Dean found in the quoted analyses of various kinds of starch 0.10—0.25 p. cent. nitrogen) and of a substance allied to cellulose, which envelopes the starch strictly so-called; according to Nägeli, it consists of two distinct compounds, which form a sort of diffusion, and of which he names that one which is soluble in saliva *granulose*, and regards the one which remains undissolved as *cellulose*; the latter substance is, however, not cellulose according to Mohl (*Bot. Zeit.* 1859, 225 and 233), who doubts the occurrence of this compound in starch-granules at all.

*Decompositions.* 1. Starch heated to  $160^{\circ}$  is changed (—according to Maschke, first into the modification soluble in hot water, then—) into dextrin. (Vauquelin & others).

It becomes coloured and froths up as the temperature is raised, and, if constantly stirred, yields a melted mass, which, at  $220^{\circ}$ — $230^{\circ}$ , consists chiefly of pyrodextrin with a little unaltered and burnt starch. (Gélis, *N. Ann. Chim. Phys.* 52, 388.) Starch dried at  $100^{\circ}$  remains unchanged at  $160^{\circ}$ , but, when heated for half an hour to  $200^{\circ}$ , it becomes brownish yellow, without appreciable loss of weight (in the same way as undried starch at  $160^{\circ}$ ), for the most part soluble in water, and its specific gravity rises to 1.555. Air-dried starch, heated in a sealed tube to  $200^{\circ}$  for an hour, or starch heated in the air to  $205^{\circ}$ — $215^{\circ}$ , is changed into a transparent, melted mass; and when in this way the maximum degree of solubility in water has been reached, it is entirely converted into dextrin. (Payen.)

Air-dried potato-starch, heated in a sealed tube in a water-bath for a day, shows no outward alteration, but does not form a paste when boiled with water; and, when this solution is left to stand, the undissolved portion soon settles down. The filtered solution treated with an equal quantity of alcohol of sp. gr. 0.833, yields a deposit, which, if collected after some hours, the spirit being allowed to drain away (while still moist, therefore (Kr.), constitutes Maschke's soluble starch: a white, salve-like, sticky mass; easily soluble in cold water, and also in dilute spirit. — When this substance is spread upon glass plates, and exposed for some hours for the spirit to evaporate, it contracts from loss of moisture, and then resembles coagulated albumin (in being a white, moist, somewhat elastic mass, but not sticky), and thereby (or when completely dried, when it has the appearance of a hard, transparent, yellow gum) loses its solubility in cold water, but is still dissolved when boiled with water. (Maschke.) Air-dried starch, heated for half an hour to  $210^{\circ}$ — $214^{\circ}$  in a sealed tube, yields the same soluble starch and dextrin; starch, dried at  $150^{\circ}$ , gives scarcely any thing but dextrin under these circumstances. (Maschke.)

Wheat-starch dried at  $100^{\circ}$  loses in six hours, at  $150^{\circ}$ — $176^{\circ}$ , 2.3 p. cent. of its weight, and becomes pale yellow; arrow-root, treated in the same way, becomes darker yellow, and loses 1.38 p. cent. (Prout.)—Starch, heated somewhat above  $100^{\circ}$ , acquires a reddish colour, smells like burnt bread, and is converted into Saussure's anidine. (Caventou.) If it is heated upon hot iron plates and moistened with water, each granule is seen under the microscope to be in motion, and to draw after itself a projecting streak of a substance soluble in water (Raspail), which, however, consists of the contents of the granule already modified. (Poggendorff, *Pogg.* 37, 116.)

2. Starch gives, by *dry distillation*, carbonic acid, carburetted hydrogen gas, water, acetic acid, and empyreumatic oil, and leaves a porous cinder.

3. In the *open fire*, it becomes soft, swells up, evolves choking vapours, and at last burns with a bright flame.

4. It is oxidized slowly by *oxygen*, more quickly by *oxygenized air*, yielding but little carbonic acid. The decomposition also takes place in the absence of light, even below  $0^{\circ}$ , also by the action of atmospheric air. (Karsten, *Berl. Akad. Ber.* 1860, 38; abstr. *J. pr. Chem.* 79, 226.) — Starch remains unchanged in *ozone* (Gorup-Besanez, *Ann. Pharm.* 110, 103; *J. pr. Chem.* 77, 407); but acquires a smell of apples. (Schönbein.) — By distillation with *peroxide of manganese, sulphuric acid, and water*, it yields carbonic acid, aqueous formic acid (Wöhler, C. G. Gmelin), and furfural. (Comp. vii. 273 and x. 370.)

5. Starch is converted by heating with *water*, first of all into paste (see *combinations*), the granules swelling up, and this by longer heating in the water-bath is transformed into soluble starch and a small quantity of dextrin (Maschke), completely into dextrin at  $150^{\circ}$  (Mitscherlich, *Pogg.* 55, 221), at  $160^{\circ}$  (Jacquelin), in general by long boiling (Payen), and at last into sugar. (Jacquelin.) — Starch remains unaltered for four months in water free from air and protected from the air at  $16^{\circ}$ , but makes the water acid, and acquires a peculiar smell if air has

access to it (Guérin-Varry); in contact with water at  $45^{\circ}$  for two days, it evolves carbonic and acetic acids (Edwards & Colin); pure starch evolves nothing, commercial starch only carbonic acid. (Guérin-Varry.) — According to Caventou, starch is partially converted into soluble amidin by boiling water, or by water at  $60^{\circ}$ — $70^{\circ}$ , and is transformed by continued boiling into starch-gum.

According to Guérin-Varry, when it is boiled from a quarter of an hour to an hour with 100—200 parts of water, *amidine tégmentaire* remains behind, while *amidine soluble* and *amidine* are dissolved, the first of which remains as a residue insoluble in cold water when the solution is evaporated. For the rest, *amidine*, which is easily and completely soluble in cold water, producing a slimy liquid, resembles starch, and has, according to Biot, a stronger dextro-rotatory power than cane-sugar. The *amidine soluble*, which remains dissolved through the agency of the *amidine*, possesses, after it has been separated again, all the properties of *amidine tégmentaire*; both resemble cellulose in properties and composition, but are not identical with it. (Guérin-Varry.)

According to Payen, when powdered starch is boiled with water, one part of its constituents is disaggregated and made more soluble than another; the less coherent parts dissolve first, then the more solid; when the maximum of solubility is reached, the formation of dextrin sets in. (Payen.)

The starch of the Trehala remains unaltered by half an hour's boiling with water; after not less than two and a-half hours' boiling it is converted into an irregularly formed mass. (Guibourt, *Compt. rend.* 46, 1213.)

A solution of starch in 500 parts water, prepared by boiling for 36 hours, remains unaltered on standing. (Jacquelain.) If it be boiled for one hour with 80 parts water, the neutral solution obtained yields a deposit on standing; in the air, becomes again turbid after 5 days, milky after 7 days; divided envelopes (of the starch-granules) may be seen in it after 14 days; after 8 months it becomes sour, smells like decaying cheese, and leaves on evaporation a residue soluble in water. (Guérin-Varry.) If starch is boiled with water for four days and the filtrate evaporated, soluble bitter gum remains behind, (Vogel, *Ann. Chim.* 82.) — Starch heated to  $140^{\circ}$  with  $\frac{3}{5}$  its weight of water, becomes coloured and soluble in water (Jacquelain); heated for half an hour to  $140^{\circ}$  with 7 parts water, it forms a mucilaginous solution. (Payen, *Comp.* also Jacquelain, *Ann. Chim. Phys.* 73, 167.)

When it is heated with water in a Papin's digester to nearly  $200^{\circ}$ , the solution contains only a little grape-sugar, but much brown bitter-sweet saccharic acid. (Gmelin.)

6. Starch distilled with sulphur gives off hydrosulphuric acid and combustible gases, and a metacetone-like liquid, but no definite sulphur-compound distils over. (Hlasiwetz, *Wien. Akad. Ber.* 5, 184.) Monosulphide of potassium and sulphide of calcium act in the same way, (Hlasiwetz.)

7. Chlorine gas, either dry or moist, does not act on starch either at the ordinary temperature or at  $100^{\circ}$ ; when it is exposed under water to the action of chlorine for 8 hours, only  $\frac{1}{20}$  is decomposed with evolution of carbonic acid. (Liebig, *Pogg.* 15, 570.) Gum behaves in the same way. (Liebig.) — Starch deliquesces, by absorbing chlorine gas, to a brown sub-



stance containing hydrochloric acid, and evolves carbonic acid. (Bouillon-Lagrange & Vogel.) — By distillation with *hydrochloric acid* and *peroxide of manganese* it yields chloral (ix. 202) also carbonic and formic acids, in quantities depending on the proportions of the materials, together with pentachlorinated propionic aldehyde (ix. 400), yellow oil and resinous matter. (Städeler, *Ann. Pharm.* 61, 101; *Handw. d. Chem. Suppl.* 1853, 796.) Starch is but slowly decomposed by *hypochlorites*. (Liebig.) Yields formate of lime when heated with 1 part *chloride of lime* and 3 parts water; but is entirely decomposed into carbonic acid and water if the chloride of lime does not contain any hydrate of lime. (Bastick, *N. J. Pharm.* 14. 20) Woody-fibre behaves in the same way. (Bastick.)

8. In the action of *nitric acid* upon starch, we have to distinguish between three different processes: a. *Formation of Xyloidin*; — b. *Formation of Soluble Starch and Dextrin*; — c. *Formation of Oxalic Acid*.

a. Cold concentrated nitric acid (sp. gr. 1.52) dissolves starch without evolution of gas; water added to the solution precipitates xyloidin as a white powder. (Braconnot, Pelouze.) If water is added immediately, nothing remains dissolved; but if the solution is allowed to stand, it gives with water less and less xyloidin, and at last none, while a substance resembling saccharic acid remains in solution. (Pelouze, *Compt. rend.* 7, 713.)

b. If starch is mixed with its own weight of concentrated nitric acid and twice its weight of ordinary nitric acid ( $NO^5_4HIO$ ) and allowed to stand for 24 or 30 hours at the mean temperature, or if it is mixed with enough common nitric acid to form a thick mud, and heated in the water-bath until red fumes are evolved, disorganised, insoluble starch is at first produced, then starch soluble in hot water, and lastly starch soluble in cold water. (Béchamp.) — Starch that has been moistened with  $\frac{1}{10}$  p. c. nitric acid and water, and then allowed to dry spontaneously, yields dextrin when heated. (Payen.) A mixture of starch with 2 p. c. nitric acid and 4 p. c. water, dried at first in the air, afterwards in a water-bath, gives with 5 parts of warm water a solution which solidifies to a jelly like lichenin on cooling, and yields sugar when boiled with acid. (Mitscherlich, *Pogg.* 55, 121.)

c. Hot nitric acid, either concentrated or dilute, employed in excess evolves nitrous gas and forms oxalic acid. (Scheele, Vauquelin); together with malic and acetic acids. (Scheele.) 8 parts of nitric acid of sp. gr. 1.34 produce 36.81 p. c. of crystallised oxalic acid. (Guérin-Varry.) — *Hyponitric acid* acting on starch neither evolves gas nor produces oxalic acid. (Bouij-Ballot, *J. pr. Chem.* 31, 211).

9. *Oil of vitriol* or *dilute sulphuric acid* converts starch into soluble starch, sulphamidonic acid, dextrin, and sugar. Heated oil of vitriol chars and destroys it, evolving sulphurous acid.

a. If starch is mixed with oil of vitriol so as to avoid heating, iodine no longer indicates its presence in the mixture (which is at first yellow, then reddish-yellow) when it has stood for half an hour or two hours. Sulphamidonic acid is produced, of varying composition according to the quantity of oil of vitriol and the duration of the action. (Fehling.) Soluble starch is formed by half an hour's action of oil of vitriol on starch. (Béchamp.)

Concerning sulphamidonic acid, see below. Saussure, by warming 1 part of starch with 3 parts oil of vitriol previously diluted with 36 parts

water, and precipitating the solution with alcohol, obtained crystals mixed with starch, which, after washing with spirit, were dissolved in a small quantity of water, reproduced by spontaneous evaporation, and freed from adhering sulphuric acid by means of alcohol. These crystals, Saussure's sulphate of starch, dissolve in water with separation of a little starch, which is coloured red by iodine. Fritzsche did not succeed in obtaining them.

b. Starch warmed with dilute sulphuric acid, loses its organized structure without dissolving; it is next gradually changed into soluble starch, and then still further into dextrin. This last is finally partly converted into sugar. (Béchamp.) The unfermentable substance itself seems to be composed of two bodies having a slight rotatory power. (Béchamp.)

The formation of sugar in this way was discovered by Kirchhoff. Sugar and dextrin are direct products of the metamorphosis of starch, and are simultaneously formed; for the formation of sugar proceeds quickly, as long as unaltered starch is present; slowly, when the acid solution is no longer coloured blue by iodine. 1 At. sugar is produced for every 2 At. dextrin. (Musculus, *N. J. Pharm.* 37, 419; *Chem. Centr.* 1860, 602.—*Compt. rend.* 54, 194; *Zeitschr. Ch. Pharm.* 5, 169.)

The formation of sugar takes place without alteration in the form of the starch-granules, of which only the actual starchy matter is decomposed. (Melsens, *Inst.* 1857, 1861.) It takes place also when the air is excluded and without evolution of gas (Vogel); when air is excluded, but with the evolution of a small quantity of carbonic acid (Döbereiner, *Schw.* 5, 281). The quantity of sulphuric acid remains unaltered by it, but the starch takes up water. (Saussure.)

The formation of sugar is complete if 100 pts. starch are boiled: (1) for some days with  $\frac{1}{2}$  pt. oil of vitriol, and 300 pts. water; (2) for 36-40 hours with 1 pt. oil of vitriol and 400 pts. water; (3) for 20 hours with  $2\frac{1}{2}$  pts. oil of vitriol and 400 pts. water; (4) for 7-8 hours with 10 pts. oil of vitriol and 600 pts. water. (Kirchhoff.)—Water containing  $\frac{1}{2}$  p. c. oil of vitriol does not produce any sugar from starch at a temperature of from 38° to 50° even after three weeks. (Daniell *Ann. Chim. Phys.* 10, 219.) 100 pts. starch afford 120 pts. syrup or 90 pts. sugar (Kirchhoff); 110·14 pts. sugar dried at 100° (Saussure); 91·52 to 115·7 pts. sugar (Guérin-Varry); 104·01 pts. (Brunner, *Pogg.* 34, 319.)

Starch granules treated with cold dilute sulphuric acid show no alteration under the microscope; with stronger acid, they swell up; still stronger acid causes a jelly to separate, at first at only one point, but afterwards the whole changes to a jelly in which the envelopes can no longer be seen; still stronger acid forms a clear solution. (Guibourt.)

The action of  $\frac{1}{4}$  pt. oil of vitriol and 2·8 pts. water upon starch at 60° causes only a few of the granules to break up; at 75° they are for the most part converted into a jelly which solidifies on cooling, and contains envelopes, some of which are partly, others entirely, opened,—also entire granules diffused through a white, powdery mass. At 90° the jelly no longer solidifies on cooling; almost all the granules are burst; and the liquid filtered at 92° or 100° leaves the torn envelopes on the filter, cemented together by dextrin: cold water extracts nothing from them; hot water gradually dissolves out the dextrin. (Biot & Persoz.) To make all the granules burst, water containing

30 p. c. sulphuric acid must be used. (Payen.)—Starch warmed with  $\frac{1}{2}$  pt. oil of vitriol and 10 pts. water forms a paste at  $70^{\circ}$ ; becomes quite fluid again at  $90^{\circ}$ , but, if quickly cooled, solidifies to a jelly, which, after washing with alcohol and drying, is insoluble in water and does not form paste, but by continued heating finally becomes quite fluid, with the exception of  $\frac{1}{10}$ , and forms a horny mass when dry.

When starch is heated to  $100^{\circ}$  with dilute sulphuric acid, the liquid still gives at first a blue colour with iodine: after half an hour iodine colours it violet; after 45 minutes, violet red; after 75 minutes, dark red; after 105 minutes, reddish brown; after 135—435 minutes pale yellowish brown. With alcohol, it gives at first a large precipitate, and, as the heating is continued, a smaller and smaller one, so that after 75 minutes, only a turbidity is produced, and after 135 minutes, no visible precipitate. The first precipitate is quite insoluble in water; those produced afterwards are more and more soluble (soluble starch) in proportion to the length of time the liquid has been heated. The rotatory power of the liquid also diminishes as the heat is continued: after 10 minutes  $[\alpha] = 216^{\circ}$  to the right; after 15 minutes,  $210.8^{\circ}$ ; after 20 minutes,  $204.3^{\circ}$ ; after 30 minutes,  $196.9^{\circ}$ ; after 45 minutes,  $179.8^{\circ}$ ; after 75 minutes,  $167.6^{\circ}$ ; after 105 minutes,  $143.6^{\circ}$ ; after 135 minutes,  $131.8^{\circ}$ ; after 165 minutes,  $96.3^{\circ}$ ; after 195 minutes,  $96.1^{\circ}$ ; after 255 minutes,  $76.5^{\circ}$ ; after 315 minutes,  $73.7^{\circ}$ ; after 435 minutes,  $73.7^{\circ}$  to the right, and remains constant if heated for a longer time; it is thus greater than the rotatory power of grape-sugar ( $[\alpha] = 66.3^{\circ}$  to the right) since the solution contains, besides the latter substance, a second optically active body, not further decomposable by acid. (Béchamp.)

If 1 part of potato-starch is heated for an hour in a water-bath with 2 pts. alcohol of sp. gr. 0.833 and a little oil of vitriol, the spirit then poured off, and the starch which lies at the bottom thoroughly washed out with water, it does not outwardly appear to have undergone much alteration, but when triturated with cold water, it imparts to the latter an organic acid, and gives a perfectly clear solution when boiled with water. The solution prepared with from 4 to 6 parts of water, solidifies to a jelly on cooling. Starch treated as above constitutes Maschke's artificial lichenin, or modified starch, which is insoluble in cold, but soluble in hot water, and is coloured blue by iodine.—The distillate obtained by boiling potato-starch with dilute sulphuric acid contains fat. (Comp. Payen, *Compt. rend.* 23, 337;—Rousseau, *Pogg.* 32, 201.)

By distilling starch (also gum or woody fibre) with oil of vitriol (phosphoric acid or chloride of tin), a volatile oil is obtained, and then formic acid (sulphurous acid? Gm.), the mass becoming carbonised. (Enmet, *Sill. Ann. J.* 32, 140; *J. pr. Chem.* 12, 120.)

a. Nitrosulphuric acid converts starch into an explosive compound corresponding to, or identical with, gun-cotton. (De Vrij, *Compt. rend.* 24, 19; comp. also Payen, *Compt. rend.* 24, 87.)

10. Phosphoric acid does not change starch into sugar. (Kirchhoff.)

11. Dilute aqueous hydrochloric acid converts starch into sugar. (Kirchhoff.)—Potato-starch,—and also rice-starch (Scharling)—when boiled with water containing hydrochloric acid, evolves, even after several days, when again heated, a smell of formic acid. Arrow-root

does not emit this odour under the same circumstances (Schmidt, *N. Br. Arch.* 19, 195), so that an admixture of 15 p. c. potato-starch in arrow-root-starch may be thus detected. (Oswald, *N. Br. Arch.* 40, 166.)—Potato-starch gives with 1·5 or 2 pts. concentrated hydrochloric acid, a tough, almost transparent mucilage, which smells of formic acid; rice-starch gives a similar product, but turbid; with dilute hydrochloric acid, potato-starch gives in 2 or 3 minutes,—rice-starch in 25 or 30 minutes,—and rice-starch containing 25 to 30 p. c. potato-starch, with hydrochloric acid of 13·5° B., in 40 or 50 seconds—a tough mucilage. (Scharling, *Ann. Pharm.* 42, 272.)

12. *Oxalic acid* converts starch into sugar. (Kirchhoff, Converchel.)—The conversion of 1 pt. starch into sugar requires 0·005 pts. oxalic acid, 1 to 12 pts. water, and that the mixture be heated to 130° for 2 hours. Starch heated to 130° with 0·005 pt. oxalic acid and 5 pts. water is converted in 20 minutes into *granules de fécule*; after an hour it is changed into dextrin, with which iodine gives a purple-red colour, and after two hours into dextrin which is no longer coloured by iodine. (Jacquelin.)—13. Starch heated for an hour to 125° with  $\frac{1}{2}$  pt. *tartaric acid* (or malic acid) and 5 pts. water is changed into gum (dextrin?). (Couverchel, *J. Pharm.* 7, 267.)

14. *Glacial acetic acid* leaves starch unaltered (Fritzche, Payen, *N. Ann. Sc. nat. Bot.* 10, 161), even on boiling (Persoz, *Compt. rend.* 17, 1067); by several hours heating to 100°, the same acid renders it partially soluble in cold, and partially soluble in hot, water (Béchamp); in 50 or 60 hours at 180°, it forms, with elimination of water, a small quantity of a compound similar to, or identical with, acetoglucose. (Berthelot, *N. Ann. Chim. Phys.* 60, 100.)—The solution obtained by heating starch with *moderately concentrated acetic acid* to 100° for 3 hours, contains, even after being heated for 28 hours, nothing but soluble starch, and has lost but little of its rotatory power. A solution in acetic acid containing 4 at. water loses, by being heated to 130° for 12 to 28 hours, 52° [ $\alpha$ ] of its rotatory power—also the property of giving a blue colour with iodine, and a precipitate with alcohol; it also leaves on evaporation an unfermentable residue. (Béchamp.)—Aqueous acetic acid produces with starch, first dextrin, afterwards sugar (Persoz), no sugar (Kirchhoff; Biot, *Compt. rend.* 17, 1067), and, after boiling, the starch-granules appear under the microscope to be covered with smooth needles (loosened and separated layers of the granule). (Fritzsche.)—In general, *warm dilute mineral acids* and *organic acids* remove from the starch-granules their starch properly so called, which turns blue with iodine, without however altering their form or structure. Granules which have been thus treated are merely coloured yellowish or reddish by iodine-water; but if moistened with iodine-water, and afterwards carefully with oil of vitriol, they are coloured blue, and in the latter case retain their form. (Melsens, *Inst.* 1857, 160.)

15. Starch slowly absorbs gaseous *fluoride of boron* at the ordinary temperature, and liquifies without becoming coloured.

16. Starch heated in a sealed tube with strong aqueous *ammonia* to 150° for several days, yields a solid, brown, gummy, deliquescent mass, having a bitter taste, easily decolorised by animal charcoal, and

precipitable from its solutions by tannin. It smells like roast meat, does not evolve ammonia by contact with solution of potash or hydrate of lime, but when fused with solid potash, yields as much as corresponds to  $2\frac{1}{2}$  to 3 p. c. nitrogen. (Schützenberger, *Zeitschr. Ch. Pharm.* 4, 65; comp. also P. Thenard, *Compt. rend.* 52, 444; *Rép. Chim. pure*, 3, 207.)

17. Starch heated to a temperature much below redness with 4 or 5 times its weight of *potash-hydrate* and a little water swells up, and forms oxalate of potash, with evolution of hydrogen (Gay-Lussac; comp. ix. 112), at the same time yielding carbonate, formiate, acetate, and propionate of potash, and in general the same products as cane-sugar yields under similar circumstances. (Gottlieb, *Ann. Pharm.* 52, 121.)—When starch is boiled for several hours with strong potash-ley, it gives at first a thick and afterwards a fluid paste, from which alcohol precipitates disorganised starch. This cannot be freed from alkali by washing with spirit, but may be obtained free from alkali by neutralising the alkaline solution with acetic acid before precipitating with alcohol. It is but slightly or not at all soluble in boiling water, becomes therewith translucent without forming a paste, and turns blue with tincture of iodine. Rotatory power  $[\alpha] = 211^\circ$  to the right. (Béchamp.)—Starch digested for 12 hours at  $50^\circ$  or  $60^\circ$  with 5 p. c. potash-ley yields dextrin. (Payen.)

Starch gives with potash-ley an opalescent solution, which does not gelatinise (Schmidt, *Ann. Pharm.* 51, 31), and has no rotatory power (Ventzke, *J. pr. Chem.* 25, 65). Potato-starch gives in  $\frac{1}{4}$  a minute with  $\frac{1}{4}$  pt. potash-hydrate and 12.75 pts. water, a very thick turbidly translucent,—wheat-starch, in half an hour, a milky,—opaque jelly;—arrow-root, a permanently fluid mixture;—the starch of the bryonia, immediately, a very thin, pale yellow, clear jelly;—kidney-bean-meal, a greenish yellow, opaque, thin,—manjok-meal, a thick, slightly translucent, mucilage, with which are mingled swollen-up granules. (Mayet, *N. J. Pharm.* 11, 81; *J. pr. Chem.* 40, 435.) In contact with a solution of 0.018 to 0.020 pt. potash-hydrate in 10 to 15 pts. water, wheat-starch remains unaltered; arrow-root forms a very turbid, and bean-starch a translucent, solid jelly. (Payen, *Compt. rend.* 48, 775.)—Starch-granules, which are insoluble in very dilute potash-ley, swell up in somewhat stronger ley (2 p. c., Béchamp), and at last dissolve without previously bursting. (Guibourt.) When alcoholic potash at  $100^\circ$  is poured over them, an air-bubble becomes apparent inside them, and does not disappear if the granules lie in the liquid for weeks; but when water is added, they absorb it and swell up greatly, so that, without the bubble of air having escaped, the space it occupied becomes invisible. (Fritzsche.)—Since the envelopes contain nitrogen, starch-granules evolve ammonia when fused with potash-hydrate. (Jacquelin.)

18. Starch deflagrates when fused with *saltpetre* and *potash-hydrate*, forming a small quantity of alkaline cyanide. (Roussin, *Compt. rend.* 47, 875.)—It is not altered by *permanganate* of potash. (E. Monier, *Compt. rend.* 46, 425; *J. pr. Chem.* 73, 479.)

19. *Soda-hydrate* decomposes starch in the same way as potash-hydrate. (Béchamp.) Starch-granules swell up in dilute soda-solution (containing 2 p. c. of soda-ley of  $25^\circ$  B) to 100 times their original bulk

without bursting; less concentrated soda-solution, than is required for old starch, suffices to make fresh starch granules, or such as have been dried over sulphuric acid in vacuo, at 120°, swell up. The presence of ammonia-salts prevents the swelling up. (Payen.)

Starch yields less oxalic acid when heated with soda-hydrate, than it does with potash-hydrate. (Possoz.) In like manner, a mixture of 1 pt. soda with  $\frac{1}{2}$ ,  $\frac{1}{3}$ , or a smaller quantity of potash, produces less oxalic acid than potash alone; but 1 pt. soda mixed with 2 or 3 pts. potash, produces more than is produced by potash alone. (Possoz.)

20. When an intimate mixture of starch with 8 pts. *quicklime* is cautiously distilled, it froths up greatly, and yields an oily distillate containing metacettone, and in smaller quantity, acetone (Fremy, *Ann. Chim. Phys.* 59, 6; *Ann. Pharm.* 15, 278).

21. *Chloride of zinc* converts starch into disorganised starch; by ebullition, into soluble starch, not into dextrin. (Béchamp.)—With 10 pts. of an aqueous solution containing 25 p. c. of fused chloride of zinc, starch gives immediately a thick paste, which does not liquefy on heating, but becomes fluid if heated for 12 or 18 hours in a water-bath, and from which alcohol precipitates disorganised starch; if, however, it has been boiled over the naked flame for 2 or 3 hours, alcohol precipitates dextrin from it. (Béchamp.)

22. When triturated in the cold, or when heated with aqueous *bichloride of tin*, it forms a compound intermediate between sugar and dextrin, or between gum and sugar, the composition of which is represented by the formula  $C^{24}H^{23}O^{23}$  (v. Payr, *Wien. Akad. Ber.* 21, 269; *J. pr. Chem.* 69, 425.)

Starch triturated with aqueous bichloride of tin, and filtered from the slight residue which remains, gives, on addition of absolute alcohol, a white precipitate, which, after being washed with absolute alcohol and dried over oil of vitriol, contains, according to v. Payr,  $C^{60}H^{64}O^{64}$ ,  $8SnO^2$ .—If the mixture is heated to 100°, alcohol causes a precipitate whose composition, when dried at 100°, is represented by  $C^{24}H^{28}O^{28}$ ,  $7SnO^2$ .—The first precipitate, suspended in water and decomposed by hydrosulphuric acid, yields bisulphide of tin, and a transparent, colourless liquid, which leaves, when evaporated in vacuo, a white pulverisable mass. This product is easily soluble in water, is not altered by iodine, and is changed into sugar when boiled with dilute mineral acids. (v. Payr.)

*White substance.*

				v. Payr.			
24 C	.....	41.02	.....	40.90	.....		
23 H	.....	6.55	.....	6.67	.....		
23 O	.....	52.43	.....	52.43	.....		
$C^{24}H^{23}O^{23}$ .....				100.00	.....	100.00	
<i>Tin-salt.</i>		v. Payr.		<i>Tin-salt.</i>		v. Payr.	
<i>a.</i>				<i>b.</i>			
60 C	..... 23.43	....	23.30	24 C	..... 15.64	....	15.50
64 H	..... 4.18	....	4.14	28 H	..... 3.04	....	3.18
64 O	..... 33.33	....	33.98	28 O	..... 24.34	....	24.24
$8SnO^2$	..... 39.06	....	38.58	$7SnO^2$	..... 56.98	....	57.08
$C^{60}H^{64}O^{64}, 8SnO^2$ ....		100.00	.... 100.00	$C^{24}H^{28}O^{28}, 7SnO^2$ ....		100.00	.... 100.00

23. Starch heated for a long time with aqueous *osmic acid*, yields carbonic acid, oxalic acid, and a peculiar acid whose ammonia-salt is soluble in alcohol. (Buttlerow, *J. pr. Chem.* 56, 271.)

24. Aqueous soluble *Prussian blue* is decolorised by starch (Vincent); by potato-starch only, not by wheat-starch (Wach, *Schw.* 51, 444), because the latter contains gluten. (Böttger, *J. pr. Chem.* 10, 110).

25. Starch heated with *Vinchona-alkaloids* evolves red vapours, which condense to a red liquid. (Batka, *Chem. Centr.* 1859, 865.)

26. In contact with *diastase*, at  $65^{\circ}$  —  $80^{\circ}$ , starch is converted into dextrin and grape-sugar, starch-granule envelopes which are no longer coloured blue by iodine remaining behind. (Payen & Persoz.) According to Payen, dextrin is formed first, and is subsequently changed into sugar; according to Balling, dextrin, dextrin-gum, and dextrin-sugar are formed one after another (*Gährungs-chemie*, Prag, 1845. 2, 15.) Starch splits up, according to Musculus (*N. J. Pharm.* 37, 419; *Chem. Centr.* 1860, 602, — *Compt. rend.* 54, 194; *Zeitschr. Ch. Pharm.* 5, 169) into 2 at. dextrin and 1 at. sugar, the first formation of the latter not being due to further alteration of the dextrin.

The transformation of starch into dextrin and sugar by means of diastase takes place without any change of volume, also *in vacuo*, also at the common temperature; by using starch-paste also at  $0^{\circ}$  (Guérin-Varry); without previous formation of gum (Trommer, *Ann. Pharm.*, 39, 360); without evolution or absorption of gas. (Payen.) It is hastened by increasing the quantity of water (Dubrunfant); by previous gelatinisation of the starch (Payen); and is complete in 3 hours at  $70^{\circ}$  —  $80^{\circ}$  with 1 pt. starch, 10 pts. water, and 0.005 pt. diastase. (Payen.) It is arrested by heating to ebullition (Payen); not interfered with by the presence, for every 100 pts. starch, of 1 pt. green vitrol, glacial acetic acid, formic acid, prussic acid, creosote, ether, sulphate of quinine, sulphate of morphine, oil of turpentine, of lemons, of anise, of cloves, or of mustard; it is slightly hindered by bicarbonate of soda, iodide of potassium, calomel, cyanide of mercury, sulphate of soda, sulphate of magnesia, acetate of lead, arsenious acid, arsenite of soda, and alum; it is much hindered by quicklime and magnesia; it is entirely prevented by tannin (Payen), bromine, soda, sulphuric acid, nitric acid, hydrochloric acid, oxalic acid, phosphoric acid, nitrate of silver, corrosive sublimate, and sulphate of copper. (Bouchardat, *Compt. rend.* 20, 107; abstr. *N. Ann. Chim. Phys.* 14, 61); it is not interfered with by small quantities of the alkaline carbonates, of acids, or of various neutral salts. (Payen & Persoz.) — Diastase can render liquid 60 times more starch than can oil of vitriol (Payen & Persoz); it can render liquid 2,000 times its own weight of starch, and in 2 hours can liquefy starch-paste mixed with chloride of sodium, even at  $-5^{\circ}$  or  $-9^{\circ}$ , without however converting it into sugar. (Guérin-Varry.)

The transformation of starch into sugar by malt (Kirchhoff), and also during the germination of grain (Saussure), is likewise due to diastase, the quantity of which becomes greater and greater as the germination of the grain proceeds, whereas dextrin and sugar are consumed. (Payen.) — The formation of sugar in the germination of

wheat, caused, according to Saussure, by a mucilaginous substance contained in it, takes place more slowly when air is excluded, and not at all in vacuo, in which case acetic, formic, lactic and carbonic acids and alcohol are produced. Concerning the action of diastase upon starch, see Traube (*Pogg.* 103, 331; *N. Br. Arch.* 96, 55).

Under the microscope, it can be seen that the envelopes of the starch-granules are not opened by the action of aqueous diastase upon starch, and hence that diastase acts by endosmose and causes the formation of sugar in the interior of the granules even at common temperatures; at 75° the envelopes are torn open, and the action of the diastase is more energetic. (Dutrochet, *Ann. Sc. Nat.* 30, 354.) No change in the form of the starch-granules takes place, it being only the starchy matter strictly so-called that is decomposed. (Melsens, *Inst.* 1857, 161.)

If the diastase-solution is heated to at least 54°, the granules burst without tearing, and the diastase then acts, not through the envelopes of the granules, but directly upon their contents; it can produce sugar only from starch-paste, not from entire starch-granules, and cannot, therefore, cause the formation of sugar from starch in germination. (Guérin-Varry.)

The quantity of sugar produced from starch by means of diastase depends on the quantity of diastase, the duration of its action, the quantity of water, and the temperature. — 100 pts. starch boiled to a paste with 1000 pts. water, and warmed to 70° — 75° for fifteen hours with 1·7 pt. diastase, gave 17·58 pts. sugar; 100 pts. starch, heated for an hour to 60° — 65°, with 3900 pts. water and 6·13 pts. diastase in 40 pts. water, gave 86·91 pts. sugar; 100 pts. starch boiled to a paste with 1393 pts. water, mixed with 12·25 pts. diastase in 367 pts. water, and kept at 20° for 24 hours, gave 77·64 pts. sugar; the same mixture in 1 hour at 0° yielded 11·82 pts. sugar (Guérin-Varry). 100 pts. starch with 25 pts. barley-malt and 4500 pts. water, yield 90 pts. sugar; the use of more malt does not increase the quantity of sugar. (Dubrunfaut.)

The examination of the products of the action of diastase upon starch at 70° — 75°, as soon as iodine no longer indicates the presence of starch, or when the diastase has acted still longer, always shows that sugar and dextrin are present in the proportion of 1 at. to 2 at. (Musculus.) It appears, therefore, that the transformation of starch by diastase does not consist in the formation first of an isomeric substance, dextrin, and the subsequent conversion of this substance into glucose by assumption of water, but in the resolution of 3 at. starch =  $3C^{12}H^{10}O^{10}$ , with assumption of  $2H_2O$ , into 2 at. dextrin =  $2C^{12}H^{10}O^{10}$  and 1 at. glucose  $C^{12}H^{12}O^{12}$ . (Musculus, *Compt. rend.* 54, 194; *Zeitschr. Ch. Pharm.* 5, 170.) Erlenmeyer (*loc. cit.*) regards this transformation as, perhaps, showing that starch, dextrin, and glucose are represented respectively by the formulæ  $C^{36}H^{30}O^{30}$ ,  $C^{24}H^{20}O^{20}$ , and  $C^{12}H^{12}O^{12}$ , and consequently that starch and dextrin are not metameric but polymeric with each other.

27. In contact with *glutin*, at a moderately high temperature, starch is converted into gum (dextrin?) and sugar. (Kirchhoff.) — Glutin renders starch-paste fluid, and causes the formation of sugar. (Bouchardat, *Compt. rend.* 20, 107; *N. Ann. Chim. Phys.* 14, 61.)



In the fermentation which takes place when starch is left in contact with gluten under water, butyric acid (x. 76), carbonic acid, and hydrogen are formed. (Erdmann & Marchand, *J. pr. Chem.* 29, 466.)

28. *Saliva* transforms starch into dextrin and sugar (*Handbuch*,\* viii. 19). (Miahle, *Compt. rend.* 20, 1485; 22, 252.—Lassaigne, *J. Chim. méd.* 21, 305 & 359; *Compt. rend.* 20, 1347.)—At  $40^{\circ}$ – $50^{\circ}$  saliva leaves starch-granules apparently unaltered, but extracts from them the true starchy matter (granulose), and leaves a residue of cellulose. (Nägeli.)—*Pepsin* deprives starch-granules of the substance which turns blue with iodine, but does not change their form or structure; the granules which remain are coloured by iodine-water from pale yellow to red, but are again coloured blue without change of form, when moistened with iodine-water and then cautiously with sulphuric acid. (Melsens, *Inst.* 1857, 161.)

29. Starch-paste is transformed into sugar by *beer-yeast* (Bouchardat); by *animal gelatin* (Kirchhoff, Matthieu de Dombasle),—by fresh, dry, powdered, or decaying gelatin (Bouchardat);—by the *gastric juice* when it contains *saliva*, not when pure (*Handbuch*, viii. 21), by the *pancreatic juice* (*Handbuch*, viii. 82 & 99) (Lassaigne, *Compt. rend.* 20, 1350; *J. Chim. méd.* 21, 309); by the substance of the *kidneys* (Marchand, *N. Br. Arch.* 52, 195; *Pharm. Centr.* 1847, 491); by *animal mucous membrane* (*Handbuch*, viii. 82), *urine*, *bile*, *semen*, *serum of blood*, and *animal tissue*; by watery infusions prepared at  $40^{\circ}$ , from the *heart*, *brain*, *lungs*, *liver*, *kidneys*, *spleen*, and *muscles*, (Magendie, *Compt. rend.* 23, 189; abstr. *N. J. Pharm.* 11, 40. (*Handbuch*, viii. 21.)

*Combinations*, a. With *Water*.—Commercial or air-dried starch retains water mechanically adhering, but no combined water; it retains no water at all when dried at  $100^{\circ}$ . (Mulder.) Starch from cereals contains 13.66 p. c. water, and potato-starch 16.41 p. c. at  $22^{\circ}$  and  $88^{\circ}$  of the hair-hygrometer (Saussure); air-dried wheat-starch contains 12.5 p. c. water (Prout), 14.2–17.8 p. c. (Wolff, *J. pr. Chem.* 71, 86); arrow-root 18.2 p. c.; air-dried starch 28 p. c. (Guérin-Varry), 21.55 p. c. (Mulder, *J. pr. Chem.* 15, 300).

Starch does not dissolve when shaken up with *cold* water, but partially when continuously triturated with it. In *hot* water it swells up and forms paste.—The formation of paste with hot water depends on its organised structure, but its insolubility in cold water does not. (Béchamp.)

Starch absorbs water when exposed to moist air. The absorption of water occurs in stoichiometrical proportions, and takes place very quickly with starch that has been previously dried at  $150^{\circ}$ , so that the starch-granules are in part torn open. (Payen.)

¶ Quantities of water absorbed, according to Nossian (*J. pr. Chem.* 83, 41), by 100 pts. of various kinds of starch, when exposed to moist air, after previous desiccation at  $100^{\circ}$ :

\* The word "Handbuch" refers to the last German edition of this work.

Variety of starch.		In air containing 73 p.c. of its maximum of moisture.	In air saturated with moisture.
Wheat-starch	absorbs ..	6.94	18.92
Rye-starch	"	10.01	19.36
Potato-starch	"	10.33	20.92
Maize-starch	"	10.53	19.55
Buckwheat-starch	"	10.85	20.02
Rice-starch	"	10.89	19.84
Acorn-starch	"	11.96	22.98

The above quantities of water correspond approximately with the formulæ  $C^{24}H^{20}O^{20}$ , 4H<sub>2</sub>O and  $C^{24}H^{20}O^{20}$ , 8H<sub>2</sub>O, which require respectively 10.00 p. c. and 18.18 p. c. water.

With most varieties of starch the absorption of moisture is complete in 5 days. (Nossian.) ¶.

Starch which has been dried at 100° — 120° becomes warm when moistened with cold water. — When potato-starch is evenly mixed up with cold water, it settles down to the bottom more quickly than wheat-starch. (Wolff, *J. pr. Chem.* 71, 86.) ¶. Wheat-starch stirred up with water, and then allowed to subside, settles down more compact than potato-starch, and is more difficult to mix up again. (Pohl, *J. pr. Chem.* 83, 40.) ¶. — Starch treated with an excess of water always takes up the same measure of it, inasmuch that 10 grm. dried starch always swell up to 14.857 cc. when covered with distilled water, 10 grm. moist starch swell up to a smaller bulk; upon this behaviour is founded the method of testing the quantity of water contained in starch by means of the *Feculometer*. (Bloch, *Compt. rend.* 39, 969; *Pharm. Centr.* 1855, 29.)

Triturated with a small quantity of cold water, starch forms a stiff mud, which hardens on drying; when starch is rubbed up for a long time with a larger quantity of water, or when powdered starch is thoroughly washed, it dissolves, all except the envelopes of the granules. (Guibourt; *Berzelius Jahresber.* 10, 201; Guérin-Varry, Jacquelin, Redwood, *Pharm. J. Trans.* 4, 505; abstr. *Rept.* 89, 84; Reinsch, *N. Jahrb. Pharm.* 3, 65; Delffs, *Pogg.* 109, 648; *N. Jahrb. Pharm.* 13, 145; Jessen, *Pogg.* 106, 497; abstr. *Rép. Chim. pure*, 1, 432, and *Pogg.* 109, 361.) — Guérin-Varry rubs air-dried starch in an agate mortar for 2 hours with 8 pts. water at 0°, then adds 40 pts. water, decants, filters, and washes the residue with water as long as the filtrate continues to turn blue with iodine. Jacquelin triturates starch for some hours with fine sand, adds water to it, mixes up the resulting mucilage with a large quantity of cold water, and filters through a threefold filter; Delffs triturates it continuously with quartz-sand and enough water to make an easily fluid mud, and filters after leaving it to subside for 24 hours. — The insoluble envelopes of the starch-granules are thus torn (Guibourt, Jessen), and the contents dissolve in water without alteration (Guibourt and others), aided, according to Knop (*Chem. Centr.* 1860, 367), by the heat resulting from the

friction. According to Wicke (*Pogg.* 108, 359) nothing is dissolved, and the filtrate merely holds starch in suspension.

Guibourt calls the aqueous starch which is held in solution *féente soluble*, and regards it as the constituent of the inside of the starch-granule, and as identical with Raspail's gum, Saussure's amidin, and Caventou's *amidon modifié*; according to Guérin-Varry, it is *amidine* mixed with *amidine soluble*, which it causes to be dissolved; Payen names it *amidon*, and Delffs *amylogen*.

The solution is clear and deposits nothing; no solid particles can be detected in it by the microscope; it gives a precipitate with alcohol (Jessen), and turns blue with iodine. A small quantity of iodine causes only a temporary blue coloration, because the iodine becomes hydriodic acid after a time; more iodine, however, colours it permanently blue. (Jacquelin.) The solution prepared from wheat-starch colours tincture of iodine pale yellow or reddish yellow, that prepared from potato-starch gives a dark blue colour under similar conditions. (Redwood.) The solution from potato-starch turns blue, while that from wheat-starch is not coloured at all, because the starch-granules of the latter are surrounded by gluten (because they are smaller than those of potato-starch, Gm.), a property which makes it possible to detect 5 p. c. of potato-starch in wheat-starch. (Marius, *N. J. Pharm.* 11, 322.)—The solution concentrated by evaporation is gummy and gelatinous when cold, and, after three days, forms an opaque mud; it dissolves partially in cold water, leaving behind an opaque jelly, which, when diluted with water, deposits a white powder, soluble in hot water. (Guibourt.)—The solution evaporated to dryness leaves a residue (transparent scales: *Jacquelin*) which is only partially soluble (scarcely soluble: *Jacquelin*) in cold water (Guérin-Varry, Payen), and also only partially soluble in boiling water, leaving behind translucent husks resembling the envelopes of the starch-granules. (Guibourt.) The insoluble portion (*amidine soluble*) amounts to 38.29 p. c.; the soluble portion (*amidine*) to 61.71 p. c. (Guérin-Varry.)—The solution preserved out of contact with the air becomes turbid in 60 hours at 20°, deposits flakes which turn blue with iodine, and are only partially soluble in hot water; after 8 months, without having fermented, it is no longer coloured blue by iodine. Even when kept so that air has access to it, the solution does not ferment; at first it turns blue with iodine, but does so no longer after 45 days. (Guérin-Varry.)—The solution cooled to 20°, and then thawed, leaves the greater part, but not all, of the *amidine soluble* (*des fibres amyglacées*, *Jacquelin*) as a white insoluble mass, while the solution contains *amidine*. (Guérin-Varry.)

The aqueous starch prepared with cold water, according to Delffs' directions (p. 93.—Delffs' amylogen), gives the following reactions: it colours solution of iodine blue, gives white precipitates with baryta-water and basic acetate of lead; reduces tartrate of potash and copper; and is without action on mercurous nitrate or terechloride of gold. (Delffs.)

Here also belongs, according to Flückiger (*Pharm. Viertelj.* 10, 40; *Zeitschr. Ch. Pharm.* 4, 104) the product obtained from starch by the following process: when starch is shaken with 10 or 20 pts. of a  $\frac{1}{2}$ — $\frac{3}{5}$  p. c. chloride-of-calcium solution, it becomes, after some time, slimy and ropy, and after 2–3 days, an upper layer separates, which is a

solution of chloride of calcium containing but little starch. The residue, shaken up with 100–150 pts. water, forms a stiff jelly, which, when filtered after the addition of more water, behaves with reagents in the same way as Delffs' amylogen, and from which alcohol precipitates flakes, which, after being washed with alcohol, dry up to colourless, transparent lumps; while moist they are easily soluble in warm water, but after being dried they are almost insoluble even in boiling water, and do not dissolve in aqueous cuprammonia (Flückiger). ¶ If a solution prepared as above is saturated with chloride of sodium, it may be kept a much longer time without alteration. (Mohr, *Lehrb. d. Chemisch-analytischen Titrimethode*, Braunschweig, 1862, 236.)

Starch triturated, first with a few drops of water, then with a concentrated solution of chloride of zinc, produces a perfect paste at the ordinary temperature. On addition of water, this paste yields a turbid liquid, which reacts with iodine like a solution of starch prepared by boiling starch with water and filtering. By precipitating the zinc with carbonate of soda and filtering, a clear solution is obtained which reacts strongly with iodine (Mohr, *Lehrb. d. Chem. analyt. Titrimeth.* 235; *Ann. Pharm.* 115, 212; abstr. *Rép. Chim. pure*, 3, 61). ¶

*Starch-paste.* — *Kleister, Colle d'amidon, Empois.* — Starch-paste is starch greatly swollen up in water (Berzelius); does not contain starch in solution (Schleiden); according to Payen, it contains, according to the quantity of water, both dissolved amidon (starch free from envelopes) and undissolved; according to Guérin-Varry, it contains dissolved *amidine* and *amidine soluble*; according to Guibourt, dissolved *fécule soluble*; according to Caventon, dissolved amidin together with unaltered starch. — It is formed when starch is heated with water to 75° — 100°; or when starch which has been moistened with cold water is mixed with boiling water. — ¶ The starch-granules of sago and tapioca are already wholly or in part in the state of paste. (Lippmann.) ¶

When starch-granules are warmed with water they split, first near the nucleus, then expand in the direction of their thinnest layers, split open either with straight or jagged edges, appear greatly expanded and transparent, and lastly, there separates from the inner layers a great number of small, soft flakes, which turn blue with iodine, whereas the swollen granules only become wine-red. (Fritzsche.) — On warming starch with water: at 54° a few of the granules, at 59° or 60° many of them, burst at the nucleus; at 61° a few, at 62° almost all, at 64° all, break up into ragged masses. (Guérin-Varry.) They first begin to burst at 56°; at 60° most of them are burst, and the bluing of the water by iodine first occurs at this temperature. The formation of paste commences at 72°, but the hot water penetrates before this by endosmose [also according to Dutrochet (*Ann. Sc. Nat.* 30, 354)], through the envelopes, into the interior of the granules, causing them to swell up to 30 times their bulk, bursting the envelopes, and making the swollen contents protrude more or less, according to the quantity of water they have taken up. The contents are partly dissolved and, on cooling, partly reprecipitated upon the envelopes, causing the paste to contract and thicken (Payen). ¶ Lippmann (*J. pr. Chem.* 83, 52) gives the following table, in which the column marked *A* shows the temperature at which the granules of the various kinds of starch

enumerated in the left-hand column begin to swell up distinctly; column *B.* the temperatures at which the formation of paste begins; and column *C.* those at which it is complete:—

	<i>A.</i>	<i>B.</i>	<i>C.</i>
Rye-starch . . . . .	45·0°	50·0°	55·0°
Maize-starch . . . . .	50·0	55·0	62·5
Horse-chestnut - starch ( <i>Æsculus</i> <i>Hippocastanum</i> ) . . . . .	52·5	56·25	58·75
Barley-starch . . . . .	37·5	57·5	62·5
Chestnut-starch ( <i>Castanea vesca</i> ) . . . . .	52·5	58·75	62·5
Potato-starch . . . . .	46·25	58·75	62·5
Rice-starch . . . . .	53·75	58·75	61·25
Starch from <i>Arum maculatum</i> . . . . .	50·0	58·75	62·5
Hermodactyl-starch . . . . .	—	61·25	65·0
Tapioca ( <i>Jatropha utilisissima</i> , Pohl) . . . . .	—	62·5	68·75
Starch of <i>Arum esculentum</i> . . . . .	45·0	63·75	68·75
Wheat-starch . . . . .	50·0	65·0	67·5
Arrow-root ( <i>Maranta arundinacea</i> ) . . . . .	66·25	66·25	70·0
Sago ( <i>Sagus Rumphii</i> ) . . . . .	—	66·25	70·0
Buckwheat-starch . . . . .	55·0	68·75	71·25
Acorn-starch . . . . .	57·5	77·5	87·5

¶

When potato-starch is warmed with water to 40° or 50°, the granules exhibit alternately dark and light rings; at 60° the granules expand, the rings separate from one another, and circles of smaller granules become apparent. At 65°—70° the granules burst, and, on boiling, appear in irregular shapes like collapsed bags. On moistening the mass with iodine, brown sheaths, consisting of cellulose, are seen in the midst of a blue, apparently granular mass. (Maschke.)—According to Guérin-Varry, triturated starch dissolves in boiling water with the exception of 2·12 p. c. envelopes (*amidine tégumentaire*); according to Guibourt, it dissolves completely by long boiling in water, and slowly only because the envelopes (which are not chemically different) are denser than the contents. According to Jacquelin, a solution prepared by long boiling with 500 pts. water contains, in the form of soluble starch, 10—17 p. c. of the starch employed.

Starch-paste forms a translucent jelly, which is thicker, the more undecomposed starch it contains. (Caventou.) Boiled with an equal quantity of water, wheat-starch gives a thinner paste than potato-starch; arrow-root, on the other hand, gives only an incoherent mucilage. (Pfaff, *N. Tr.* 11, 2, 197.) Common starch-paste is sticky, not so that prepared from rice-starch (Vogel); it has a faint taste, and a peculiar smell when prepared from wheat-starch, not when prepared from arrow-root. (Oswald, *N. Br. Arch.* 40, 166.) The starch of *Æsculus Hippocastanum* does not form a paste, but only a thick mucilage. (Schweigger-Seidel, *J. pr. Chim.* 5, 227.)

Starch-paste becomes acid by standing in the air, owing to the formation of lactic acid (Braconnot),—of an uncrystallisable acid. (Collard de Martigny, *J. Chim. méd.* 3, 238.) If saturated with common salt, it may be kept in stoppered bottles without alteration for more than a year. (Mohr.) Starch is converted by boiling into sugar (which, after 1 or 2 months at the common temperature, amounts to  $\frac{1}{3}$ — $\frac{1}{2}$  of the starch used), into gum, into slightly altered

pasty starch (*amidine*), and sometimes into a resinous substance (Comp. Saussure, *Ann. Chim. Phys.* 11, 388 and Caventou).

When exposed to *sunlight*, starch-paste is changed, first into a substance resembling inulin, then into dextrin and sugar.—The transformation does not take place in the dark, except in presence of potassio-ferric tartrate, the presence of which makes sunlight act with one-third more energy; nitrate of uranium renders the action of sunlight from 3 to 10 times more intense; ferrous lactate or citrate and corrosive sublimate, on the other hand, diminish or prevent it altogether. (Nièpce de St. Victor & Corvisart, *Compt. rend.* 49, 368; abstr. *Ann. Pharm.* 113, 112.)

B. *With Iodine*.—Starch is coloured blue by contact with iodine, and forms iodide of starch (Colin & Gaultier de Claubry), a dark blue shining, easily pulverizable mass, retaining the original form of the starch-granules. (Fritzsche; Schacht, *N. Br. Arch.* 47, 164.) It is to be regarded as starch coloured blue by the surface of the granules being covered with finely divided iodine. (Liebig, *Ann. Pharm.* 42, 308; and others.) According to Payen and Fritzsche, it is a compound of 10 at. starch with 1 at. iodine.—According to the way in which it is prepared, iodide of starch may contain from 3.2 to 7.1 p.c. iodine.—The colour of the compound is not the same with all kinds of starch: arrow-root starch gives the purest blue; wheat-starch more of a reddish violet colour. (Pohl.)

The formation of iodide of starch takes place also when air is excluded. (Payen.) It also takes place slowly when starch is triturated with solid iodine, tincture of iodine, or an ethereal solution of iodine; it occurs immediately in presence of water, or when warm tincture of iodine is poured on the starch. Iodine-vapour, or iodine dissolved in absolute alcohol, does not form iodide of starch with dry starch. (Payen; Goble, *J. chim. méd.* 20, 121; Langlois.) ¶. Potato-starch, treated with alcohol and tincture of iodine, is coloured more or less brown; otherwise the same phenomena occur as when pure alcohol is used. The blue coloration occurs only when a great excess of water is added, or when the alcohol has become dilute by evaporation and absorption of water. These phenomena are accounted for by the solvent power of alcohol for iodine being great enough to overpower the attraction of the starch for iodine. (Pohl, *J. pr. Chem.* 83, 37.) ¶ — Starch-paste mixed with iodide of potassium is coloured blue by all re-agents which liberate iodine from metallic iodides, and hence by chlorine (Lassaigne; Böttger, *Ann. Pharm.* 33, 338; Wackenroder, *N. Br. Arch.* 47, 166), fuming nitric acid (Walthier, *Qu. J.* 3, 378; Harting, *J. pr. Chem.* 22, 46), bromine (Wackenroder), ozone (Schönbein, *Pogg.* 75, 356), oil of vitriol, sesquichloride of iron, and many other bodies. Very dilute peroxide of hydrogen separates iodine either not at all, or very slowly, from a mixture of iodide of potassium and starch; it acts quickly, however, if, free acid being avoided, a small quantity of a dilute aqueous ferrous salt is added. (Schönbein, *Pogg.* 112, 281.)

The blue coloration of starch either does not occur or is less pure in presence of tannic acid, a small quantity of gallic acid, pyrogallie acid or urine (Löwe, *J. pr. Chem.* 74, 358); in presence of saliva, blood-serum, and other substances, it is not produced until the liquid containing the starch has been mixed with 1—2 drops of tincture of

iodine, then with a few drops of aqueous potash, and, lastly, supersaturated with nitric acid. (Béchamp, *N. J. Pharm.* 27, 406.)

Starch is perceptibly coloured blue by  $\frac{1}{2000.000}$  pt. of aqueous iodine, not by  $\frac{1}{200.000}$  pt. (on the contrary: Stromeyer, *Gillb.* 49, 146); by chlorine in presence of  $\frac{1}{200.000}$  pt. iodine in the form of iodide of potassium (Lassaigne); by a small quantity of fuming nitric acid in presence of  $\frac{1}{100.000}$  pt. iodide of potassium, very faintly in presence of  $\frac{1}{300.000}$  pt.; in the last case the coloration is prevented by chloride of potassium if the quantity of this salt present amounts to 10,000 times as much as the iodide of potassium (Walther); it is produced in presence of  $\frac{1}{200.000}$  pt. iodine in the form of iodide of potassium, after some hours with  $\frac{1}{450.000}$  to  $\frac{1}{550.000}$  pt. iodine in the same form; not at all with a still smaller quantity. (Harting.) A solution of starch-paste containing from  $\frac{1}{300.000}$  pt. to  $\frac{1}{600.000}$  pt. iodine, as iodide of potassium, is coloured blue at 0° on addition of sulphuric acid containing hyponitric acid; whereas, at 13°, the coloration is barely perceptible with  $\frac{1}{330.000}$  pt., at 20° with  $\frac{1}{264.000}$  pt., at 30° with  $\frac{1}{132.000}$  pt. iodine. Hence it results that the quantity of iodine required to colour aqueous starch-paste increases with the temperature. (Fresenius, *Ann. Pharm.* 102, 184; *Kopp's Jahresber.* 1857, 581.)

Pure iodide of starch is obtained: 1. By adding iodine or alcoholic tincture of iodine to a filtered solution of starch-paste in concentrated hydrochloric acid, washing the resulting precipitate with water, till the liquid runs away colourless, and drying over oil of vitriol. (Fritzsche.) — The compound thus prepared generally contains hydrochloric acid (Fritzsche, Böttger.) — 2. By mixing potato-starch paste containing iodide of potassium with an equivalent quantity of chlorine-water, and washing and drying the precipitate, which forms immediately. (Böttger.) Lassaigne triturates potato-starch with cold water, dilutes, washes, mixes the filtrate (which contains Lassaigne's amidin) with aqueous or alcoholic iodine, and evaporates in vacuo. Lassaigne's iodamidin thus prepared contains 41·76 p. c. iodine.

Duroy (*Compt. rend.* 51, 1031; *Zeitschr. Ch. Pharm.* 4, 88), who regards blue iodide of starch as coloured by excess of iodine, obtains his colourless iodide of starch—which, however, may be blued by chlorine or nitric acid—by boiling aqueous blue iodide of starch till it is decolorised, or by leaving it in contact with washed beer-yeast, and evaporating the decolorised solution. He frees the residue by alcohol from the sugar which has been formed, colourless iodide of starch then remaining in the form of a sweet gum.

Iodide of starch heated in a retort becomes first darker, then lighter, yields a distillate of aqueous hydriodic acid, acetic acid and empyreumatic oil, and leaves a residue of charcoal. (Pelletier.) Air-dried iodide of starch heated in a sealed tube to 162°, melts completely to a transparent, brownish-yellow mass, which becomes vitreous on cooling, dissolves in boiling oil of vitriol, and is precipitated therefrom in brown flocks by water. (Payen; comp. Jacquelin.)

Iodide of starch, whether dry or dissolved in water, is decolorised by exposure to sunlight (Raspail, Guibourt, Payen); the colour is restored by ozone (Schönbein, *Pogg.* 75, 354).

Iodide of starch behaves like starch when agitated or triturated with water. — If it has been prepared from aqueous starch or in the manner above described, it dissolves readily in cold water, and is obtained unaltered by spontaneous evaporation, or by evaporation in

vacuo. (Fritzsche; Jessen, *Pogg.* 100, 497; and others.) It is precipitated from the aqueous solution by alcohol less easily than aqueous starch (Jessen); by isinglass, acids, and salts, and by cooling (Payen). The easily-formed solution of Lassaigne's iodamidin in cold water retains its blue colour unaltered for 4 years, and solidifies at 5° to a dark blue mass, which, when thawed, deposits dark blue flocks soluble in water at 55° to 60°. Seput (*N. J. Pharm.* 21, 202) obtained an iodide of starch soluble in cold water, by heating 1 pt. iodine with 3 pts. starch to 80°—100° for half-an-hour, and then heating it, with agitation, to 130°—140°. Magnes-Lahens (*N. J. Pharm.* 19, 243) obtained it by heating the same mixture in the water-bath for two or three hours, and washing out the excess of iodine with alcohol. The product thus obtained is called by Seput *iodide of dextrin*.

A very dilute aqueous solution of iodide of starch, heated to 65° (Payen & Persoz), becomes colourless, but recovers its blue colour on cooling, provided it has not been boiled long enough to expel all the iodine. With 100 pts. of boiling water, iodide of starch forms a colourless paste (Pelletier), which gives off the vapour or odour of iodine (Fritzsche). Decolorised iodide of starch is free from hydriodic acid (Pelletier, Fritzsche), contains iodic acid (Langlois), and hydriodic acid (Lassaigne), and is therefore again blued by chlorine and by concentrated mineral acids, even if it remains colourless on cooling (Langlois, Pelletier); also by salts (Payen), not by vegetable acids or by dilute mineral acids, sulphurous acid, or carbonic acid (Pelletier). A concentrated aqueous solution of iodide of starch is not decolorised by boiling (Langlois; comp. Jacquelin).

The decoloration of aqueous iodide of starch by heat is due to the volatilisation of the iodine; hence it does not take place (with concentrated iodide of starch) in a sealed tube, or when the liquid contains excess of iodine. If the iodine which evaporates on boiling be expelled by blowing air into the vessel, the iodide of starch remains colourless after cooling, but if it can reabsorb the iodine-vapours on cooling, the colour is restored. Dilute iodide of starch heated 30 or 40 times in a sealed tube is decolorised by each application of heat, but regains its blue colour on cooling, without much decrease of intensity. (Bandrimont, *Compt. rend.* 51, 825; *Zeitschr. Ch. Pharm.* 4, 27; — comp. Pohl, *J. pr. Chem.* 83, 88.)—This statement does not accord with the observations of Kraut. When aqueous iodide of starch, which became colourless on being heated in an open tube, was enclosed in a sealed tube and immersed in the water-bath, decoloration took place as quickly as in an open vessel. Iodide of starch, which had been heated in a closed tube for a short time only, became blue again on cooling, but not that which had been heated for several hours. On adding more iodine after cooling, the blue colour was restored; on sealing the tube and again heating, it was destroyed; and on cooling, the colour was restored or not restored, according to the duration of the heating. At the same time hydriodic acid was produced, recognisable by cyanide of mercury. (Kr.) Decoloration of iodide of starch or its aqueous solution is produced by all re-agents which cause the iodine to enter into combination, especially by chlorine, the colour being then restored by zinc and dilute sulphuric acid (Henry & Humbert, *Compt. rend.* 47, 298); nitric acid, which converts the iodine into iodic acid, and destroys the starch (Langlois; Wackenroder, *H. Br. Arch.* 47, 166); sulphurous acid,



hydrosulphuric acid (Langlois); arsenious acid (Pisani); aqueous ammonia and potash (Pelletier), the blue colour being then restored by acids. Iodide of starch is likewise decolorised by terchloride of antimony, chloride of arsenic, terchloride of gold, ferrous, manganous, stannous, mercurous, mercuric, and silver salts. (Pisani.) Infusion of galls decolorises iodide of starch: hence certain roots containing both starch and tannin, are not blued by iodine till after addition of nitric acid. (Wackenroder.) Decoloration is also produced by pyrogallic acid, by wood-vinegar and by tobacco-vapour, after the compound has been moistened with acetic acid. (Löwe, *J. pr. Chem.* 71, 353.) Slightly blued starch is decolorised by fixed oils. (Payen.) Alcohol and ether abstract part of the iodine from iodide of starch. (Payen, Langlois.)

When starch-paste is mixed *a* with tincture of iodine, *b* with iodide of potassium, and both or only the latter with nitric acid free from nitrous acid, and bromine-vapour is made to flow on to the surface of both mixtures, *a* is completely decolorised, but *b* assumes an emerald-green colour, changing to olive-green on further exposure to the bromine-vapour, and finally to brown. The latter colouring is also produced by chlorine or hyponitric acid, whereas the mixture of iodide of potassium and starch-paste (not containing free nitric acid) is not coloured emerald-green either by these re-agents or by bromine-water. (J. Reinsch, *N. Jahrb. Pharm.*)

C. *With Bromine.*—*Bromide of Starch.*—Formed by precipitating a solution of starch in hydrochloric acid with aqueous bromine.—Orange-yellow powder, which cannot be dried without loss of bromine; it loses its colour from above downwards, even while in the acid liquid, and is completely decolorised, with loss of bromine, by heat, but re-assumes a pale yellow colour on cooling. (Fritzsche.)

D. *With Acids.*—*Sulphamidonic acid* (p. 104).

E. *With Bases.*—*Amilate of Baryta.*—By precipitating starch-paste with baryta-water. (Payen.)—Aqueous chloride of barium does not form any precipitate. (Payen.)—When baryta-water is boiled with potato-starch for half-an-hour, thick white lumps of amilate of baryta separate on cooling. (Zeise.)—Coherent precipitate becoming very tenacious after a while (Payen); it dissolves after some time in the precipitating liquid (Payen), or in water if washed for some time with that liquid, and is precipitated from the solution by baryta-water. (Zeise.)

*Amilate of Lime.*—By precipitating thin starch-paste with lime-water. (Braconnot, *Ann. Chim. Phys.* 4, 372; Payen.) White flocks. (Braconnot.) Boiling starch-paste mixed with a few drops of aqueous chloride of calcium and a small quantity of aqueous potash sometimes throws down amilate of lime in the form of a jelly. (E. Schmidt, *Ann. Pharm.* 51, 31.)

Starch-paste dissolves recently precipitated *phosphate of lime*. (Vauquelin, *J. Phys.* 85, 126; Schmidt.)

*Amilate of Lead.*—*Basic.* 10 pts. of starch are boiled with 1200 pts. of water; the liquid is filtered; the boiling filtrate mixed with 20 pts. of ammonia previously diluted with 40 pts. of water; the liquid added, with stirring, to a solution of 30 pts. neutral acetate of lead in 200 pts. water and 5 pts. ammonia; the supernatant liquid

decanted from the precipitate after the lapse of an hour, and the precipitate is treated four times with boiling water—being each time left to settle and the liquid decanted in close vessels—then washed on the filter with boiling water, pressed between bibulous paper, and dried in vacuo first over hydrate of potash, then, after pulverization, at 180°. (Payen.) When aqueous starch free from ammonia is precipitated with ammoniacal aqueous solution of neutral acetate of lead, the precipitate contains a smaller quantity of lead-oxide (54.73 to 56.45 p. c. according to Payen); similarly when it is precipitated by a solution of basic nitrate of lead and the precipitate dried in vacuo at 100° (28 p. c.). (Berzelius.) Aqueous starch is also precipitated by basic and neutral acetate of lead without the aid of ammonia (Caventou); not by the neutral acetate. (Thomson, Trommsdorff.)

				Payen. at 180°.
24 C .....	144.0	....	19.1	.... 19.40
18 H .....	18.0	....	2.4	.... 2.37
18 O .....	144.0	....	19.2	.... 19.35
4 PbO .....	446.8	....	59.3	.... 58.88
<hr/>				
C <sup>24</sup> H <sup>18</sup> Pb <sup>4</sup> O <sup>20</sup> .2PbO ? .....	752.8	....	100.0	.... 100.00

Payen regards the compound as C<sup>24</sup>H<sup>18</sup>O<sup>9</sup>.2PbO, according to which formula, it should give up 1 at. HO at 180° in exchange for PbO. Since, however, starch-paste heated with 2 pts. oxide of lead, first to 140°, then to 180° in vacuo, gives off only traces of water, Mulder (*J. pr. Chem.* 15, 300) is of opinion that the oxide of lead, in combining with the starch, cannot take the place of water. Payen's compound of starch with oxide of lead dried at temperatures below 130° still contains unaltered starch and traces of dextrin, turns yellow at 160°, lemon-yellow after some time at 179°, gives off only 0.5 p. c. water between 129° and 179°, but contains together with the unaltered starch a larger quantity of dextrin (Berzelius).—It is not converted into dextrin at a temperature of 170°—180°, and it is only after addition of acid that it swells up in hot water, is blued by iodine, or converted by diastase into sugar (Payen).

*Solution of borax* coagulates starch-paste (Höfer), not in presence of free acid or of tartrate of potash. (Löwig, *Org. Verb.* 1, 374.)

Aqueous *nickel-ammonia* neither causes starch to swell up nor dissolves it. (Schlossberger, *Ann. Pharm.* 107, 22; *J. pr. Chem.* 73, 370.)

Aqueous *ferric sulphate* does not precipitate starch-paste (Payen); starch-paste also prevents the precipitation of ferric salts by alkalis. (II. Rosc.)

Starch is insoluble in *aqueous basic sulphate* or *hyposulphate of cuprammonia* (Schweizer, *J. pr. Chem.* 72, 111), even when heated, but swells up strongly therein (Schlossberger, *Ann. Pharm.* 107, 23; *J. pr. Chem.* 73, 370). The power of the solution to make starch swell up is limited; its action extends from without inwards, and causes the swollen starch-granules to appear darker than the surrounding liquid. (Cramer, *Chem. Centr.* 1858, 57; *J. pr. Chem.* 73, 13.)—When aqueous sulphate of cuprammonia is poured upon wheat-starch, the granules swell up strongly, and an insoluble violet compound (*amilate of copper*) is formed, containing 12.75 p. c. cupric oxide, ammonia slowly decolorises it, and removes the copper. When cold dilute acids are poured upon this compound, it swells up strongly, and finally dissolves with the exception of the enlarged envelopes of the starch-granules. (Payen, *Compt. rend.* 48, 67.)

Starch boiled with water forms a precipitate with aqueous *nitrate of silver*; this precipitate is more copious with arrow-root than with

potato-starch. (Schmidt, *N. Br. Arch.* 19, 195.) Starch boiled with 90 pts. water dissolves nitrate of silver. (Thomson.)

Starch-paste prepared with 1 pt. starch to 90 pts. water does not precipitate: *cobalt-salts, zinc-salts, stannous, ferrous, ferric, or cupric salts, nitrate of lead, mercuric nitrate, terchloride of gold, or bichloride of platinum.* (Thomson.) Starch-paste prepared with 1 pt. wheat-starch and 50 pts. water does not precipitate: *uranic nitrate, manganous sulphate, tartar-emetie, nitrate of zinc, chloride of calcium, chloride of tin, sesquichloride of iron, the salts of cobalt, nickel, copper, or silver, mercuric nitrate, terchloride of gold, chloride of platinum, or chloride of palladium.* (Trommsdorff, *Taschenb.* 1824, 24.) Thin starch-paste heated to  $50^{\circ}$ , does not precipitate aqueous acetate of alumina or ferrous sulphate, but produces a slight turbidity in mercurous nitrate.

*Infusion of galls* added to thin starch-paste produces an abundance of grey flocks (Thomson; Payen & Persoz), which are partially decomposed and leave a residue of starch when completely washed with alcohol (Thomson); and also when washed with cold water. (Kalinowsky, *J. pr. Chem.* 35, 201.) The flocks disappear on heating the liquid above  $49^{\circ}$ , reappear below  $49^{\circ}$ , and dissolve in excess of the infusion of galls. (Thomson.) If the infusion of galls be slowly added, they dissolve at first, but not afterwards; they are likewise insoluble in a large quantity of water, and are deposited on adding more of the infusion of galls. (Payen.) The dried precipitate is brownish yellow, translucent, brittle, and has a harsh taste. (Thomson.) Tasteless. (Kalinowsky.)

Starch is insoluble in *alcohol*, in *ether*, and in *oils*, both *fixed* and *volatile*. From impure starch, these solvents remove chlorophyll, wax or fat.—Starch swells up when glycerin is poured upon it. (Cap & Garot, *N. J. Pharm.* 26, 81.)

### *Appendix to Starch.*

## 1. Béchamp's Soluble Starch.

Distinguished by Béchamp, as a substance differing from common starch and from dextrin. He regards it as identical with the substance originally called dextrin by Biot (not that to which the name dextrin is now applied). Respecting Maschke's soluble starch, see page 82.

*Formation.* Common starch is converted into soluble starch by hot dilute acids, diastase, concentrated acids, either cold or hot, and solution of chloride of zinc.—When starch is subjected to the action of dilute acids or of diastase, it is first disorganised, then converted into a substance which is not immediately blued by iodine (Saussure's *Ligneux amylicé*), then into a substance which dissolves only in water at  $80^{\circ}$ , and separates again as the solution cools [Jacquelin's *Granules de fécule*, Schulze's *Amidulin* (*J. Pr. Chem.* 44, 178)], and finally into soluble starch.—Soluble starch is produced, without previous disorganisation, by the action of glacial acetic acid on starch. (Béchamp.)—It is likewise obtained by treating xyloïdin with aqueous protochloride of iron. (Béchamp, *Compt. rend.* 37, 134.)

*Preparation.*—Starch-paste is subjected to the action of diastase or of dilute sulphuric acid, till the mixture is coloured by iodine, no longer blue but violet, the liquid is then saturated with carbonate of baryta, or the action of the diastase is interrupted by boiling, the filtrate is precipitated with alcohol, and the precipitate is washed with alcohol and dried.—2. One part of starch is heated with 4 pts. glacial acetic acid to  $100^{\circ}$  in a sealed tube for six hours, and the contents of the tube are washed on a filter with alcohol, and dried.—3. Starch covered with 2 pts. of ordinary and 1 pt. of fuming nitric acid, is left to stand in a covered vessel at  $18^{\circ}$  —  $20^{\circ}$ , till it is converted into a clear, transparent mass,—or a thick mixture of starch and nitric acid is heated till it gives off red vapours; alcohol is added in either case; and the insoluble residue is washed with alcohol, and dried over oil of vitriol.—4. Three parts of starch are triturated with 2 pts. oil of vitriol; the stiff white paste is covered with alcohol after the lapse of half-an-hour; and the insoluble residue is purified by washing with alcohol, solution in water, and precipitation with alcohol.—¶. 5. Nitramidin, binitramidin, or one of the compounds isomeric therewith (pp. 106—112), is heated with a rather dilute and perfectly neutral solution of protochloride of iron, keeping the temperature below  $100^{\circ}$ , and adding iron filings to prevent the formation of free hydrochloric acid, which would transform the starch into dextrin. As soon as the evolution of nitric oxide ceases, the liquid is quickly cooled, filtered, mixed with alcohol, and left to stand for twenty-four hours. It then deposits an ochreous mixture of starch and ferric oxide, which is washed with alcohol and dissolved in water; the filtered solution is treated with excess of baryta, and the resulting precipitate of amilate of baryta is washed with water containing a little baryta, then suspended in water and decomposed by carbonic acid. The colourless filtrate, concentrated and freed from dissolved carbonate of baryta by heating in the water-bath, is then mixed with very strong alcohol, which precipitates the starch in very minute granules, to be purified by repeated washing with nearly absolute alcohol, and drying in vacuo over oil of vitriol. (Béchamp, *N. Ann. Chim. Phys.* 64, 329.) ¶.

*Properties.* White powder, or if obtained by evaporating the aqueous solution, gummy transparent mass. If prepared with glacial acetic acid, it does not differ in appearance from ordinary starch.—Rotatory power  $[\alpha] = 211^{\circ}$  to the right. (Béchamp; Berthelot, *N. Ann. Chim. Phys.* 48, 495.)

				Béchamp. at $20^{\circ}$ .	
24 C.....	144	.....	44.44	.....	44.34
20 H.....	20	.....	6.17	.....	6.44
20 O.....	160	.....	49.39	.....	49.22
<hr/>				<hr/>	
$C^{24}H^{20}O^{20}$ .....	324	.....	100.00	.....	100.00

By the further action of the dilute acids or of the diastase used in its preparation, it is converted into dextrin, sugar, and non-fermentable amylin; by oil of vitriol or chloride of zinc, it is little, if at all, converted into dextrin and sugar.

Soluble starch dissolves readily in water, whether hot or cold;—the solution is not rendered turbid by cooling or by evaporation to a

syrup; neither does it suffer any alteration of rotatory power by keeping.

Soluble starch in the solid state or in solution, is turned blue by *iodine*, forming soluble iodide of starch. It is precipitated from its solution by *lime* or *baryta-water*, by *alcohol*, and by *tannin*. (Béchamp.)

## 2. Sulphamidonic Acid.

FEHLING. *Ann. Pharm.* 55, 13.

BLONDEAU DE CAROLLES. *Rev. scient.* 15, 69; abstr. *J. pr. Chem.* 33, 439; *Ann. Pharm.* 52, 416.

Known chiefly in combination with bases.—By the action of oil of vitriol upon starch, compounds are produced, containing, according to the quantity of the oil of vitriol, the duration of the action, and the limits within which the temperature is restrained, from 12 to 44 at. C, and 12 to 39 at. H and O, to 2 at. sulphuric acid. See the baryta-salts. (Fehling.) The product obtained by 8 or 10 days' action of oil of vitriol on starch contains dextrin and sugar as well as sulphamidonic acid.

The *aqueous acid* is obtained by decomposing the lead-salt with sulphuretted hydrogen. On evaporating the filtrate separated from the sulphide of lead in vacuo at  $10^{\circ}$ , there remains a white, non-crystalline, acid, deliquescent mass, whose concentrated solution blackens at  $100^{\circ}$ , and decomposes readily, even at ordinary temperatures, with formation of sulphuric acid, dextrin, and sugar. (Fehling.)

If the solution obtained by adding starch to oil of vitriol and diluting with water, be neutralised with alkaline or metallic carbonates, the *sulphamidonates* are produced. These salts are amorphous, swell up and give off vapours of sulphuric acid when heated; are decomposed by chlorine with formation of hydrochloric acid; and dissolve readily in water. (Blondeau.)

*Sulphamidonate of Baryta*.—When the solution obtained by adding starch to oil of vitriol and diluting with water, is neutralised with carbonate of baryta, and the filtrate is evaporated in a current of air at  $25^{\circ}$ , non-crystalline baryta-salts remain, which, after drying in vacuo, may be heated to  $100^{\circ}$  for three or four hours without alteration, dissolve easily in water, and are decomposed when heated therewith, depositing sulphate of baryta. These baryta-salts differ in composition according to the quantity of oil of vitriol used, and the time during which it has remained in contact with the starch.

a. By 12 hours' action of  $2\frac{1}{2}$  pts. oil of vitriol on 1 pt. starch =  $C^{12}H^{10}O^{11}, SO^3.BaO, SO^3$ .—b. By 24 hours' action of the same =  $C^{16}H^{10}O^{11}, SO^3.BaO, SO^3$ .—c. By 3 hours' action of  $1\frac{1}{2}$  pts. oil of vitriol on 1 pt. starch =  $C^{20}H^{15}O^{16}, SO^3.BaO, SO^3$ .—d. By 24 hours' action of 2 pts. oil of vitriol on 1 pt. starch =  $C^{24}H^{20}O^{20}, SO^3.BaO, SO^3$ .—e. By 48 hours' action of  $1\frac{1}{2}$  pts. oil of vitriol on 1 pt. starch =  $C^{28}H^{24}O^{24}, SO^3.BaO, SO^3$ .—f. By 48 hours' action of  $2\frac{1}{2}$  pts. oil of vitriol on 1 pt. starch =  $C^{32}H^{26}O^{26}, SO^3.BaO, SO^3$ .—g. By 72 hours' action of  $1\frac{1}{2}$  pts. oil of vitriol on 1 pt. starch =  $C^{36}H^{30}O^{30}, SO^3.BaO, SO^3$ .—h. By 60 hours' action of  $2\frac{1}{2}$  pts. oil of vitriol on 1 pt. starch =  $C^{40}H^{30}O^{32}, SO^3.BaO, SO^3$ .—i. By

1½ hours' action of 1½ pts. oil of vitriol on 1 pt. starch =  $C^{44}H^{36}O^{38}$ ,  $SO^3 \cdot BaO, SO^3$ . (Fehling.)

Fehling.  
Dried at 100°.

	a.	b.	c.	d.	e.	f.	g.	h.	i.
C.....	22.28	25.25	28.19	29.82	31.62	33.61	31.68	35.27	35.2
H .....	3.80	3.87	4.32	4.40	4.86	4.99	5.15	4.92	5.4
O .....	—	29.42	30.73	33.41	35.38	—	—	—	—
SO <sup>3</sup> .....	—	10.56	9.46	8.27	7.18	—	—	—	—
BaO, SO <sup>3</sup> ....	35.30	35.90	27.30	24.10	20.96	19.87	16.65	17.17	15.1
	100.00	100.00	100.00	100.00					

*Sulphamidonate of Lime.*—By saturating the solution of starch in oil of vitriol with carbonate of lime, and evaporating the filtrate.

a. After the oil of vitriol had acted for some time on the starch =  $C^{28}H^{24}O^{24}, SO^3 \cdot CaO, SO^3 \cdot 2HO$ ; resembles gum arabic. (Blondeau de Carolles).—b. After a mixture of 1 pt. starch and 2 pts. oil of vitriol had been immediately diluted with water, saturated with carbonate of lime, the filtrate evaporated to a syrup, and precipitated with a large quantity of alcohol, and the resulting viscid precipitate washed with alcohol and dried in vacuo; c. after the mixture had stood for 24 hours; d. after it had stood for 7 days, and been treated like b. =  $C^{32}H^{22}O^{32}$ ,  $CaO, S^2O^5$  (Kalinowsky); but according to Gerhardt (*N. J. Pharm.* 8, 309),  $C^{24}H^{23}CaO^{24}, 2SO^3$ .

## Blondeau de Carolles.

## v. Kalinowsky.

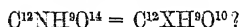
	a.		b.	c.	d.
	at 30°—40° in vacuo.		Over oil of vitriol in vacuo.		
C .....	29.49	.....	34.43	.....	34.94
H .....	5.22	.....	5.64	.....	5.70
O .....	43.61	.....	37.61	.....	37.76
CaO .....	5.68	.....	5.65	.....	5.20
SO <sup>3</sup> .....	16.00	.....	16.67	.....	16.40
	100.00	.....	100.00	.....	100.00

*Sulphamidonate of Lead.*—Obtained by immediately saturating the solution of starch in oil of vitriol with carbonate of lead, of the composition a =  $C^{36}H^{36}O^3, SO^3 \cdot PbO, SO^3 \cdot 2HO$ ; but if the solution is left for 36 hours before saturation, the salt has the composition b =  $C^{24}H^{24}O^{24}, SO^3 \cdot PbO, SO^3 \cdot 2HO$ . (Blondeau de Carolles.)

## Blondeau de Carolles.

	a.	b.
	at 30°—40° in vacuo.	
C .....	28.31	24.98
H .....	5.00	4.48
O .....	40.23	36.81
PbO .....	15.40	14.11
SO <sup>3</sup> .....	11.06	19.62
	100.00	100.00

## 3. Nitramidin.



BRACONNOT (1833). *Ann. Chim. Phys.* 52, 290; *Pogg.* 29, 176; *Ann. Pharm.* 7, 245; abstr. *Schw.* 68, 368.

LIEBIG. *Ann. Pharm.* 7, 249.

PAYEN. *N. Ann. Sc. nat. Bot.* 10, 161.

PELOUZE. *Compt. rend.* 7, 713; *J. pr. Chem.* 16, 168. — *Compt. rend.* 23, 890; *J. pr. Chem.* 40, 200.

GLADSTONE. *Mem. Chem. Soc.* 3, 412. — *Pharm. J. Trans.* 13, 215.

BOUJES-BALLOT. *Scheik. Onderzoek.* Utrecht, No. 3; *J. pr. Chem.* 31, 309; *Ann. Pharm.* 45, 47.

BÉCHAMP. *N. Ann. Chim. Phys.* 46, 338; abstr. *Compt. rend.* 41, 817; *J. pr. Chem.* 68, 61. — Further, *N. Ann. Chim. Phys.* 64, 311.

*Explosive Starch, Xyloïdin. Pyroxam, Amidon mononitré, Fécule nitrique, Fécule mononitrique.*

Discovered and named by Braconnot in 1833; examined by Pelouze and more recently by Béchamp.

*Formation.* 1. By the action of strong nitric acid of sp. gr. 1.52 (or of red fuming nitric acid: *Liebig, Gladstone*), on starch in the cold (Braconnot, Pelouze). Starch is likewise converted into nitramidin by nitric acid of sp. gr. 1.414, but not by weaker acid. (*Gladstone*.) — Béchamp has shown that there are two modifications of nitramidin, one insoluble or nearly so in ether-alcohol, acetone and wood-spirit; the other (isonitramidin) soluble in those re-agents. The production of one or the other of these modifications depends chiefly on the temperature, nitramidin being produced when the liquid is kept cool; isonitramidin when the temperature is allowed to rise. If the product is left too long in contact with the acid, it is destroyed and converted into an acid, probably saccharic acid. This effect had been observed by Pelouze, who attributed it to the presence of an excess of nitric acid; but according to Béchamp, an excess of acid has no influence on the result, unless the starch is very dry, and the acid very highly concentrated, in which case a certain quantity of binitramidin is produced. — 2. By the action of strong nitric acid on glycogen. (Pelouze, *Compt. rend.* 44, 1321; *J. pr. Chem.* 73, 249.)

A product agreeing in composition and properties with nitramidin is formed when wood-shavings, linen, or cotton is heated with strong nitric acid. (Braconnot, Payen.) Strong nitric acid of sp. gr. 1.5 dissolves cotton at 30° — 35°, forming a thick transparent gum, from which water throws down nitramidin. (De Vrij, *Compt. rend.* 24, 19.) The identity of these products with nitramidin appears doubtful. (Kr.)

*Preparation.* Starch is dissolved in cold concentrated or fuming nitric acid, the gummy solution is immediately mixed with water, and the tenacious transparent precipitate is washed with water and well dried. (Braconnot, Béchamp.) — The starch should be quickly and intimately mixed with fuming nitric acid, by triturating it in small portions in a glass mortar, and the translucent gelatinous solution immediately diluted with water, whereby coarse-grained nitramidin is produced. (Ballot.) — ¶. 1 pt. of starch dried at the temperature of the air (20°), is mixed with 5 to 8 pts. of fuming nitric acid, by tritu-

ration in a thick porcelain mortar (to avoid rise of temperature), till it is reduced to a perfectly transparent semifluid mass without any trace of granules, and 20 to 30 pts. of water are added at once, the trituration being constantly kept up. The compound then separates in the form of a curdy precipitate, easily pulverized under water. It is washed with distilled water, and dried at the temperature of the air or in a hot-air chamber. (Béchamp.)

To purify this product, it is dissolved in a cold mixture of 10 pts. glacial acetic acid and 1 pt. bihydrated acetic acid [ $C^4H^4O^4, 2HO$ ; sp. gr. 1.073]; the solution is filtered, distilled water gradually added, the viscous mass which falls to the bottom is separated from the supernatant liquid by decantation, and a larger quantity of water is added; a pulverulent precipitate is then formed, which must be collected on a filter, washed and dried. (Béchamp.) ¶

*Properties.* White powder. Coarse-grained (Ballot); sandy, consisting of tough opaline vesicles (Reinsch, *N. Repert.* 3, 181). Tasteless. (Braconnot, Liebig.) Has a scarcely perceptible bitter taste. (Reinsch.) Neutral. (Braconnot.) Poisonous. (Baker Edwards, *Chem. Centr.* 1849, 48.) Rotatory power of nitramidin  $[\alpha] = 155.96^\circ$  to the right.

Calculation according to Laurent and Béchamp.				Béchamp.	Gladstone.	Bouij's- Ballot.	Petten- kofer.
				mean.		mean.	
12 C	72	...	34.78	...	34.53	...	36.76
N	14	...	6.76	...		...	5.65
9 H	9	...	4.34	...	4.35	...	4.79
14 O	112	...	54.12	...		...	52.80
$C^{12}NH^9O^{14}$				...	207	...	100.00
				...	100.00	...	100.00

According to Pelouze and others, it is  $C^{12}NH^9O^{14}$  or  $C^{12}H^9O^9, NO^5$ ; according to Laurent (*N. Ann. Chim. Phys.* 19, 374) it is  $C^{24}XH^{18}O^{20}$  or  $C^{24}X^2H^{18}O^{20}$ . Ballot concludes, from its reaction with alkalis (*vid. inf.*), that it is a mixture of two different substances.

¶ Béchamp has shown (*N. Ann. Chim. Phys.* 64, 316) that the product formed by the action of nitric acid on starch has, for the most part, the composition  $C^{12}NH^9O^{14}$  or  $C^{24}N^2H^{18}O^{28}$ , but that when the starch is very dry and a large excess of acid is used, a certain quantity of binitramidin may likewise be formed: *a.* 5 grammes of starch dried at  $20^\circ$  (corresponding to 4.5 grm. dried at  $100^\circ$ ) trituated with 20 grm. of nitric acid (obtained by distilling 1 at. of dry nitrate of potash with rather more than 2 at. strong sulphuric acid) yielded a product weighing 5.76 grms.—*b.* 5 grms. of the same starch, trituated with 50 grms. of the same nitric acid, yielded 5.95 grms. of product dried in vacuo.—*c.* 5 grms. starch, dried at  $100^\circ$  and 40 grms. nitric acid yielded 5.78 grms. product dried in vacuo.—*d.* 5 grms. starch, dried at  $20^\circ$  and 60 grms. nitric acid yielded 5.7 grms. product dried in vacuo.—*e.* 5 grms. starch, dried at  $100^\circ$ , and 60 grms. nitric acid yielded 7.24 grms. product dried in vacuo.—The experiments *a*, *b*, *c*, *d*, give, as a mean result, 125.7 pts. of nitramidin for 100 pts. of starch,  $C^{12}H^{10}O^{10}$  or  $C^{24}H^{20}O^{20}$ . The quantity calculated from the formula  $C^{12}NH^9O^{10}$  or  $C^{24}N^2H^{18}O^{20}$  is 127.8.—In the last experiment, *e*, the increase of weight is much more considerable, probably in consequence of the formation of a more highly nitrated compound.

Béchamp regards nitramidin and the three compounds next to be described, as nitrates corresponding in constitution to the nitric ethers (assigning to nitramidin, for example, the formula  $C^{12}H^9O^9, NO^5$ ), and not as products analogous to nitrobenzene, &c.: 1. Because, when heated with reducing agents—ferrous-acetate, for example,—they yield, not amidated products, in which  $NO^4$  is replaced by  $NH^2$  [*e.g.* aniline  $C^{12}H^5(NH^2)$  from nitrobenzene  $C^{12}H^5(NO^4)$ ], but soluble starch (p. 102), a compound free from nitrogen; just as the nitric ethers, when treated in like manner, reproduce the corresponding alcohols.—2. Because, when they are dissolved in strong sulphuric acid and the

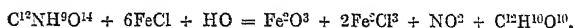


solution is diluted with water and distilled, aqueous nitric acid passes over, not accompanied by red vapours.—3. Because the optical rotatory powers of these compounds, as determined by observation, are nearly the same as those which calculation would assign to mixtures of an active molecule of hypothetically anhydrous starch  $C^{12}H^8O^8$ , with the inactive molecules  $HO, NO^5$  in nitramidin and  $2NO^5$  in binitramidin. [For the details of these calculations see the original memoir (*N. Ann. Chim. Phys.* 64, 341.).] ¶.

*Decompositions.* 1. *Spontaneous decomposition.* Nitramidin, after being kept for six years, suddenly began to give off gases, including hydrocyanic acid, and after a few weeks left a small quantity of a turbid liquid. (Gladstone.) According to Béchamp, it may be kept without alteration for an indefinite time.—2. Nitramidin detonates slightly when heated (Braconnot), giving off a small quantity of nitrous acid (Liebig), not by pressure or percussion (Pelouze). When heated on paper, it does not melt, but becomes carbonised, without setting fire to the paper. (Braconnot.) It takes fire at  $180^\circ$  (Pelouze), at  $182^\circ$  (Gladstone).

According to Béchamp's earlier experiments, it takes fire between  $180^\circ$  and  $190^\circ$ , leaving a large quantity of charcoal; according to his later experiments, it begins to give off red vapours at  $198^\circ$ , when heated in a test-tube, and deflagrates slowly between  $198^\circ$  and  $200^\circ$ , leaving a black residue, without leaving any charcoal. (Pelouze.)—Nitramidin subjected to dry distillation gives off a yellow distillate containing acetic acid, leaving charcoal amounting to  $\frac{1}{3}$  of its weight. (Braconnot, Pelouze.)

3. Nitramidin is dissolved by *nitric acid* of sp. gr. 1.25, or higher. The solution in nitric acid of sp. gr. 1.414 acquires a yellowish red colour, and after some days no longer deposits xyloidin on addition of water, but contains an acid similar to saccharic acid (xi. 513), which is likewise formed on boiling starch with strong nitric acid, and is easily transformed by heat into a black acid, which, when boiled with nitric acid, is converted into oxalic acid, without evolution of carbonic acid. (Pelouze, Payen.)—Nitramidin dissolved in fuming nitric acid separates as pyroxylin, on mixing the solution with an equal volume of oil of vitriol. (Cottureau, *Compt. rend.* 24, 305.) ¶ From Béchamp's experiments, it appears probable that the product thus obtained is not pyroxylin but binitramidin (p 110) ¶. With *oil of vitriol*, nitramidin forms a colourless solution, from which it is not precipitated by water (Braconnot); this solution easily and quickly decolorises solution of indigo, and gives off nitrous gas when treated with copper. (Liebig.)—5. Nitramidin treated with a warm aqueous solution of *protochloride of iron*, gives off nitrous gas, and is converted into soluble starch. (Béchamp.)



In contact with *ferrous sulphate*, it exhibits the coloration characteristic of nitrates. (Cottureau, *Compt. rend.* 23, 1157.)

6. Nitramidin is not dissolved by aqueous *alkalis* (Pelouze, Béchamp); becomes translucent and glutinous when immersed therein. (Braconnot.)—According to Ballot, it dissolves partially. The portion soluble in weak aqueous alkalis (not in ammonia) contains, after precipitation with acetic acid and washing of the flocculent precipitate with the same acid, 38.01 p. c. C. and 4.94 H. ( $C^{12}H^9NO^{12}$ ); the insoluble portion which sinks to the bottom, and, after careful washing, appears white and pulverulent, contains 36.94 p. c. C. and 4.51 H. ( $C^{12}H^9NO^{12}$ ).—Nitramidin after thorough washing with alcohol, and then with weak aqueous potash, contains 37.32 p. c. C. and 5.17 H. (Ballot.)

*Combinations.* Nitramidin is insoluble in *water*. (Braconnot, Pelouze.) It softens in boiling *water*. (Braconnot.) It decolorises alcoholic tincture of *iodine*, forming a yellow compound. (Braconnot.)

It dissolves in strong *hydrochloric acid*, especially when heated (Braconnot, Gladstone), with rapid decomposition (Béchamp). It is nearly insoluble in pure *glacial acetic acid*, but dissolves easily in that acid mixed with  $\frac{1}{10}$  of the bihydrated acid,  $C^4H^4O^4 \cdot 2HO$ . (Béchamp, *N. Ann. Chim. Phys.* 64, 320.) When moderately heated with *glacial acetic acid*, it dissolves to a thick mucus, which coagulates on addition of *water*, and leaves a colourless varnish when evaporated (Braconnot). Xyloïdin prepared from cotton separates, when precipitated from its solution in *acetic acid*, as a coagulated mass; that prepared from starch separates in the form of a powder. (De Vrij.)

Nitramidin is insoluble in aqueous *ammonia*. (Braconnot, Ballot.)

It does not dissolve in *alcohol*, *ether* (Braconnot, Béchamp), or *ether-alcohol* (Béchamp). With anhydrous *ether* it forms a jelly which dries up on evaporation to a white opaque film. (Schönbein; Böttger, *Pogg.* 70, 820.)—Xyloïdin prepared with *nitric acid* dissolves in *ether*; that which is prepared with a mixture of *nitric* and *sulphuric acid*, dissolves in *ether-alcohol*. (Flores Domonte & Ménard, *Compt. rend.* 23, 86). Nitramidin is insoluble in *chloroform*, *acetic ether* and *benzene*, slightly soluble in *wood-spirit*. In *acetone* it appears to soften, but does not dissolve. (Béchamp.)

#### ¶ 4. Isonitramidin.



BÉCHAMP. *N. Ann. Chim. Phys.* 64, 320.

*Fécule mononitrique soluble, Fécule isomomonitrique*

*Formation and Preparation.* The same as for nitramidin (Béchamp), excepting that the *nitric acid* must be present in greater excess, and the temperature allowed to rise. Starch triturated with 10 or 12 times its weight of fuming *nitric acid* in a rather thick glass vessel, so that the heat developed by the reaction may not be too quickly dissipated, is converted in six or eight minutes into a yellow, slightly viscid, perfectly transparent liquid, which, when poured into 30 times its volume of *water*, yields a precipitate less curdy and more pulverulent than nitramidin precipitated in like manner. It is purified by dissolving it in *ether-alcohol*, filtering, and leaving the *ether* to evaporate. It is then deposited as a pulverulent mass, which may be dried in a hot-air chamber.

*Properties.* White powder. Rotatory power (determined on the *acetic acid* solution),  $[\alpha] = 156.96^\circ$  to the right.

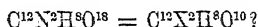
					Béchamp.
12 C	.....	72	...	34.78	..... 35.46
N	.....	14	...	6.76	..... 6.71
9 H	.....	9	...	4.34	..... 4.44
14 O	.....	112	...	54.12	..... 53.39
<hr/>					
$C^{12}NH^9O^{14}$	....	207	...	100.00	..... 100.00

Respecting the rational constitution, see page 107.

*Decompositions.* At ordinary temperatures it may be preserved indefinitely without alteration. A sample prepared in 1854 has been preserved unaltered up to the present time (summer of 1859), in the climate of Montpellier. Heated in a tube, it begins to give off red vapours at  $170^{\circ}$ , and deflagrates at about  $172^{\circ}$ , leaving a small quantity of white matter. By *protochloride of iron*, it is decomposed in the same manner as nitramidin, yielding soluble starch. (p. 108.)

*Combinations.* Insoluble in *water*. More soluble than the preceding in *glacial acetic acid*. In *alcohol* of 95 per cent., and in *ether* it does not dissolve, but merely softens; but in a mixture of *ether* and *alcohol* containing excess of the former it dissolves with great facility. Slightly soluble in *nearly absolute alcohol*; insoluble in *chloroform*; easily soluble in *acetone*, *acetic ether*, and *methylic alcohol*. The solubility of the compound in certain menstrua appears to vary with the temperature at which it is prepared; the product to which the preceding statements apply was prepared at  $20^{\circ}$ ; but another product prepared at  $34^{\circ}$  with 1 pt. of starch dried at that temperature and 10 pts. of fuming nitric acid, dissolved easily in alcohol of 95 per cent.

## ¶ 5. Binitramidin.



BÉCHAMP. *N. Ann. Chim. Phys.* 64, 322.

*Dinitramidin, Nitroxyleidin, Fécule dinitrique.*

*Formation.* 1. By the action of oil of vitriol on the mononitrated compounds isobinitramidin being formed at the same time.—2. Occasionally together with nitramidin, by treating dry starch with excess of nitric acid (see experiment e. p. 107).

*Preparation.* 1 pt. of starch dried at  $20^{\circ}$  is dissolved in 12 pts. of fuming nitric acid, and the solution, filtered if necessary through pounded glass, is placed in a freezing mixture and quickly mixed with 8 pts. oil of vitriol, whereupon the mixture soon becomes turbid and deposits a soft white, very bulky mass. The whole is then quickly poured into a large quantity of cold water, care being taken to divide the solid mass and mix it up well, so as to avoid any great rise of temperature in particular parts. The product, which is a white powder resembling nitramidin, but more finely divided, is freed from sulphuric acid by washing with a large quantity of water, then dried in the hot-air chamber.

The product is chiefly a mixture of binitramidin and isobinitramidin mixed, however, with small quantities of the mononitrated compounds.—Two experiments gave 147 and 150 pts. of dried product from 100 pts. of starch; according to the formula  $C^{12}N^2H^8O^{18}$  it should be 155.6.—To separate the two binitrated compounds, the dried powder is treated with alcohol of 96 p. c. first in the cold, then at  $40^{\circ}$ , which dissolves the isobinitramidin and leaves the binitramidin. The latter, after washing with alcohol, is

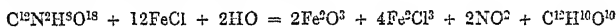
dissolved in ether containing alcohol, and the filtered solution is evaporated, either in the open air, or in an air-bath heated to 25° or 30°.

*Properties.* White mass easily pulverized.

Béchamp.						
12 C .....	72	...	28.57	...	27.7	..... 29.6
2 N .....	28	...	17.11			
8 H .....	8	...	3.17	...	3.47	
18 O .....	144	...	51.15			
<hr/>						
C <sup>12</sup> N <sup>2</sup> H <sup>8</sup> O <sup>18</sup> .....	252	...	100.00			

According to Béchamp, the rational formula is C<sup>12</sup>H<sup>8</sup>O<sup>8</sup>.2NO<sup>5</sup>.

*Decompositions.* 1. Binitramidin is much more disposed to *spontaneous decomposition* than mononitramidin, giving off red fumes a few days after its preparation.—2. When heated in a test-tube, it begins to give off red vapours at 175°, emits them in abundance between 175° and 178°, and deflagrates rapidly with a hissing noise at the last-mentioned temperature, leaving only a small quantity of white matter.—3. Mixed with pounded glass and subjected to *dry distillation* in a combustion-tube connected with a cooled U-tube, it gives off: *a.* A gaseous mixture containing at different stages of the distillation from 61 to 42 p. c. nitric oxide, from 11 to 23 p. c. carbonic acid, from 29 to 27 p. c. carbonic oxide, a small quantity of nitrogen, and at the commencement of the distillation hydrocyanic acid, the disengagement of which however ceases at an early stage; —*b.* An acid liquid, which has a disagreeable odour of tobacco-smoke, and quickly reduces nitrate of silver, especially with the aid of heat; —*c.* Charcoal, which forms a shining deposit on the inner surface of the tube.—4. Binitramidin is reduced by *ferrous salts* in the same manner as nitramidin, yielding soluble starch:



*Combinations.* Insoluble in *water*, and in *alcohol*, but soluble in pure *ether* and in *alcoholised ether*. Soluble in *glacial acetic acid*, but insoluble in a mixture of the glacial acid and the bihydrated acid, being in this respect exactly opposite to monitramidin (p. 109). Soluble in *acetone*, *acetic-ether*, and *wood-spirit*: insoluble in *chloroform*, *hydrosulphuric ether*, and *methylic alcohol*.

## ¶ 6. Isobinitramidin.



BÉCHAMP. *N. Ann. Chim. Phys.* 64, 322.

*Isodinitramidin, Fécule isodinitrique.*

This compound is produced, together with binitramidin, by the process described at page 110, and is separated from the latter by alcohol of 96 p. c. which dissolves it. On mixing the alcoholic filtrate with water, the compound separates as a very fine white powder, which agglomerates during desiccation, and then becomes strongly

electric by trituration. If the alcohol be evaporated by heat, the isobinitramidin separates in transparent laminae.

Rotatory power.  $[\alpha] = 131.5^\circ$ .

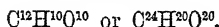
					Béchamp.
12 C	.....	72	....	28.57	..... 30.40
2 N	.....	28	....	11.11	..... 10.72
8 H	.....	8	....	3.17	..... 3.25
18 O	.....	144	....	57.15	..... 55.63
$C^{12}H^8O^{18}$ .... 252					.... 100.00

$C^{12}H^8O^{18}, 2NO^5$  according to Béchamp (p. 108).

*Decompositions.* 1. Isobinitramidin is even more subject than binitramidin to *spontaneous decomposition*.—2. *Heated* in a test-tube, it begins to give off red fumes at  $170^\circ$ , and deflagrates like the preceding compounds at  $172^\circ$ , leaving only a small quantity of white matter.—3. By *protochloride of iron*, it is reduced like the preceding compounds, yielding soluble starch.

*Combinations.* Insoluble in *water*, soluble in *alcohol* of 96 p. c.; dissolves with difficulty in *ether*, but easily in a mixture of *ether and alcohol*. With *acetic acid*, *acetone*, *acetic ether*, *chloroform*, *methylic alcohol*, *amylic alcohol*, and *hydrosulphuric ether*, it behaves like binitramidin. (Béchamp) ¶.

## Inulin.



VALENTIN ROSE (1804). *A. Gehl.* 3, 217.

JOHN. *Chemische Schriften*, 4, 73.

GAULTIER DE CLAUDRY. *Ann. Chim.* 94, 200.

PAYEN. *J. Pharm.* 9, 288.—*Ann. Chim. Phys.* 26, 102; *Repert.* 18, 53; *Ann. Sc. nat. Bot.* 1840, 91.

STRATINGH. *Repert.* 21, 418.

MULDER. *Ann. Pharm.* 28, 278; *J. pr. Chem.* 15, 299.

PARNELL. *Ed. Mag. J.* 17, 126; *Ann. Pharm.* 39, 213; *J. pr. Chem.* 26, 140.

CROOCKWIT. *Ann. Pharm.* 45, 184; abstr. *J. pr. Chem.* 28, 316.

WOSKRESENSKY. *Petersb. Acad. Bull.* 5, No. 3; *J. pr. Chem.* 37, 309.

BOUCHARDAT. *Compt. rend.* 25, 274; abstr. *Pharm. Centr.* 1847, 782.

TH. ANDERSON. *N. Ed. Phil. J.* 7, 136; *J. pr. Chem.* 47, 449.

THIBAUT. *N. J. Pharm.* 25, 205; *J. pr. Chem.* 62, 253; *Pharm. Centr.* 1854, 336.

DUBRUNFAUT. *Compt. rend.* 42, 803; *J. pr. Chem.* 69, 208; *Inst.* 1856, 174.

*Helenin* (John); *Alantin*, *Menyanthin* (Trommsdorff); *Dahlin* (Payen); *Synanthrin Sinistrin* (Marquart, *Ann. Pharm.* 10, 92.)—Braconnot's *Datiscin* was formerly erroneously regarded as inulin.—Discovered by Val. Rose in 1804.

*Sources.* According to Mulder and Woskresensky, inulin is a

universally distributed constituent of plants, and is found especially in the roots of *Inula Helenium* (Rose), *Angelica Archangelica* (not in this root, according to Buchholz and Buchner), *Anthemis Pyrethrum* (John), *Colchicum autumnale* (Pelletier & Caventou), *Leontodon taraxacum* (Mulder, Herberger, *Repert.* 52, 399; Frickinger, *Repert.* 73, 45), *Cichorium intybus* (Woskresensky); in the tubers of *Dahlia pinnata* (not in spring, according to Woskresensky), (Payen), *Helianthus tuberosus* (Braconnot); in the stalks of *Solanum Dulcamara*, in spring, not in autumn (Jonas, *N. Br. Arch.* 42, 130); in the buck-bean, *Menyanthes trifoliata* (Trommsdorff); in morel (a kind of fungus) Beltz; in *Lerp-manna* (from *Eucalyptus dumosa*) to the amount of 13.8 per cent. (Anderson.)—*Lichen fraxineus* and *Lichen fastigiatus* contain, according to Berzelius, inulin, lichenin, or a substance of similar character.—The seeds of *Helianthus annuus* contain a non-fermentable substance, insoluble in cold water and in alcohol, which, after boiling with dilute acids, reduces copper from an alkaline solution, probably inulin.

*Preparation.* A. *From Elecampane-roots.*—The roots are boiled with a large quantity of water, the decoction is evaporated, the extract exhausted with cold water, and the inulin which remains undissolved is washed. (Gaultier, Stratingh.)—The roots are exhausted with hot water in a displacement apparatus; the concentrated infusion is evaporated to 10° or 12° Bm. and mixed with 2 pts. alcohol, and the inulin thereby precipitated is purified by reprecipitation with alcohol from its concentrated solution, and decolorised with animal charcoal. (Thibault.)—Köhnke (*N. Br. Arch.* 39, 289) boils elecampane-roots (previously exhausted with alcohol) with water; evaporates the filtered extract to  $\frac{1}{3}$  or  $\frac{1}{4}$ ; mixes it with alcohol till it becomes turbid; collects the pale yellow inulin which separates after several days; and purifies it by dissolving it in hot water, and washing the inulin which separates on cooling with warm alcohol.—The helenin mixed with inulin prepared from elecampane-roots is extracted by boiling with alcohol. (Croockwit.)

B. *From Potatoes or Dahlia-tubers.*—1. The pulverulent deposit which separates in the cold from the expressed juice of potatoes is dissolved in hot water, and the solution is filtered, evaporated and left to cool, whereupon it deposits inulin. (Braconnot.)—2. The nearly transparent juice expressed from dahlia-tubers is left to stand for some hours, whereupon it solidifies, from separation of inulin, to a stiff paste, which is to be washed and dried. (Ludwig, *N. Br. Arch.* 82, 163.)—3. Dahlia-tubers rubbed to a pulp are washed on a hair sieve in a thin stream of water, as long as the liquid continues to run through milky, and the inulin which separates from it on standing, is collected—or in case it is slow in settling down, the turbid liquid is heated till it boils; the coagulated vegetable albumin is skimmed off; and the remaining liquid is left to cool; it then, after a few days, deposits a thick pulp easy to wash. (Liebig, *Ann. Pharm.* 2, 235.)—Roots of *Dahlia pinnata* treated in this manner do not yield any inulin; but this substance settles down as a white powder when the aqueous extract of the fresh tubers, cut in slices, dried and pulverized, is evaporated, and the extract diluted with water. (Wittstein, *Repert.* 71, 362.)—4. Dahlia-tubers rubbed to a pulp are washed with cold water on a linen or woollen cloth; the residue is boiled for half-an-hour with 2 pts. water and a small quantity of chalk;

			Payen.		Mulder.		Parnell.
			<i>at 150°</i>	<i>at 170°</i>	<i>at 120°</i>	<i>at 120°</i>	<i>air-dried.</i>
			<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
24 C .....	144	...	44.44	...	44.19	...	43.87
20 H .....	20	...	6.17	...	6.17	...	6.40
20 O .....	160	...	49.39	...	49.64	...	50.23
<hr/>			<hr/>				
C <sup>14</sup> H <sup>20</sup> O <sup>20</sup> ..	224	...	100.00	...	100.00	...	100.00

	Croockwit.		Woskresensky.		Anderson.	Dubrunfaut.
	at 120°—160°		at 100°—120°		at 150°	at 100°
	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>	<i>k</i>	<i>l</i>
C .....	43·37	43·48	52·18	49·59	44·03	44·32
H .....	6·23	6·25	6·86	6·86	6·30	6·19
O .....	50·40	50·27	40·96	43·55	49·67	49·49
	100·00	100·00	100·00	100·00	100·00	100·00

*a* Normal; *b* soluble inulin from Iceland moss; *c* from dandelion-, *d* from elecampane-root; *e*, *f* and *g* from dahlia-tubers; *h* from chicory-roots; *i* from dandelion-roots, partially oxidised; *k* from Lerp-manua.

Corresponds to the formula  $C^{24}H^{20}O^{20}$  (Payen, Mulder, Dubrunfaut);  $C^{24}H^{20}O^{21}$  (Parnell);  $C^{24}H^{19}O^{14}$  (Woskresensky); that prepared from dahlia-tubers corresponds to the formula  $C^{24}H^{20}O^{21}$ ; from elecampane roots, to  $C^{24}H^{20}O^{20} \cdot \frac{1}{2}HO$  (Croockwit). The composition of inulin varies with its origin and mode of preparation (Croockwit), because it is oxidised by the joint action of heat and water (Woskresensky); it is always the same. (Dubrunfaut.)

*Decompositions.* 1. Inulin dried at 100° does not lose weight at 180°, but towards 190° it turns yellow, and melts with slight loss of weight and some decomposition. (Dubrunfaut).—It melts at a temperature somewhat above 100° (Braconnot); at 168°, with colouring and loss of weight, and becomes insoluble in water and in alcohol (Payen); forms a sweet mass, easily soluble in water (Braconnot).—When fused at a gentle heat, it gives off water, and, after cooling, forms grey scales, which may be rubbed to a white powder. (Gaultier).—2. In the open fire, it melts and volatilises in white pungent vapours smelling like burnt sugar, and leaves a small quantity of charcoal (only if it contains gum, according to Braconnot); at a stronger heat, it burns with a light blue flame. (V. Rose).—3. By *distillation* it yields brown empyreumatic acetic acid, but no free empyreumatic oil. (Rose, Braconnot.)

4. When heated with water to 100°, it is slowly but completely converted into non-crystallisable (Dubrunfaut), lævo-rotatory (Bouchardat), fermentable sugar (Croockwit).—The transformation takes place after 15 hours' boiling (Croockwit); after 1½ hours' digestion of inulin with water, the filtrate, which gives but a slight precipitate with strong alcohol, leaves sweet gum when evaporated. (Woskresensky). It is not altered by prolonged boiling with water (Braconnot); by repeated boiling with water it becomes gummy (John); somewhat soluble in water and alcohol (Payen).

5. By boiling with *nitric acid*, inulin is converted into malic, oxalic, and acetic acids, not into mucic acid.—Its solution in fuming nitric acid is not precipitated by water. (Croockwit).—6. By oil of vitriol, it is turned yellow, then brown, and is ultimately carbonised. (Payen).—Inulin boiled for 12 hours with  $\frac{1}{25}$  pt. oil of vitriol and a large quantity of water, yields a small quantity of bitter-tasting sugar (Gaultier), digested with  $\frac{1}{10}$  oil of vitriol and a large quantity of water at 75°, it yields uncrystallisable, fermentable sugar, soluble in alcohol of sp. gr. 0·823, and sweeter than starch-sugar; with dilute phosphoric acid, a still sweeter sugar is obtained; with  $\frac{1}{10}$  acetic acid, a sugar of inferior sweetness. (Payen.)

*Dilute acids* convert inulin into sugar, both in the cold and when



heated (Payen, Braconnot, Dubrunfaut, Bouchardat); the transformation is not attended either with evolution or with absorption of gas.

7. Aqueous *arsenic acid* dissolves inulin with aid of heat; after continued action, the cooled solution no longer deposits inulin, and leaves on evaporation a rose-coloured mass, which afterwards becomes darker and finally black, grape-sugar being first formed, then humic and formic acids. (Baumann, *N. Br. Arch.* 37, 264.)

4. *Oxide of lead* converts inulin wholly or partially into glucic acid, which, if afterwards exposed to the air, changes into apoglucic acid. A warm aqueous solution of inulin reduces other salts of lead, copper, and silver. If an ammoniacal solution of lead is precipitated by aqueous inulin, the filtrate separated from the white precipitate deposits spangles of lead after a few hours, and contains formic acid. (Croockwit.)

9. Inulin is not *fermentable*. (Bouchardat.)—Neither the aqueous solution nor inulin suspended in water ferments in contact with yeast, or with tartaric acid and yeast. (Dubrunfaut.)—Inulin suspended in water together with yeast ferments like sugar, but much more slowly, giving off carbonic acid, alcohol, and a small quantity of ammonia (Payen), but only if it has been previously converted into sugar by the action of unwashed sour yeast. (Bouchardat.)

10. *Diastase* alters neither the rotatory power nor the other properties of inulin. (Payen.)—Inulin is digested in the stomach, and does not pass, as inulin, either into the urine or into the fæces. (Bouchardat.)

*Combinations. With Water.*—A. *Hydrated Inulin.*—Gummy inulin immersed in water swells up, absorbs water, and crumbles to dull-looking granules of  $\frac{1}{20}$  millimetre diameter, which do not exhibit the double refraction of starch.—Inulin kept in moist air at  $10^{\circ}$  acquires a specific gravity of 1.361; gives off 11.25 p. c. water in dry air at  $10^{\circ}$ , and 4.75 p. c. more at  $100^{\circ}$ . (Dubrunfaut.)—Inulin which has been dried in the hot-air chamber absorbs water and becomes opaque on being immersed in water. (Payen.)—Rotatory power =  $26.16^{\circ}$  to the left (Bouchardat);  $29.46^{\circ}$  (Dubrunfaut.)

				Dubrunfaut.	
$C^{12}H^{20}O^{20}$ .....	324	...	85.72		
2 HO .....	18	...	4.76	...	4.75
4 HO .....	36	...	9.52	.....	11.25
<hr/>					
$C^{12}H^{20}O^{20}, 6HO$ .....	378	...	100.00	.....	

B. *Aqueous Inulin.*—Inulin is insoluble in cold water (Rose); nearly insoluble (Braconnot); slightly soluble (Parnell); soluble in 500 pts. water at  $0^{\circ}$  (Payen); in 200 pts. at  $10^{\circ}$  (Dubrunfaut), in 240 pts. between  $12^{\circ}$  and  $18^{\circ}$  (Biltz), in 50 pts. at mean temperature (although vegetable sap contains about 12 p. c. of the soluble modification, which changes into insoluble inulin only on standing). (Bouchardat.) It dissolves in  $\frac{1}{2}$  to  $\frac{1}{4}$  pt. water at  $60^{\circ}$  (Gaultier), abundantly in water at  $66^{\circ}$  (Dubrunfaut), easily in hot water (Parnell).

A hot aqueous 10 per cent. solution of inulin does not deposit any thing on cooling, but after standing for 12 to 24 hours, it deposits such a

quantity of inulin, that from 4 to 5 p.c. still remains in solution, and separates but imperfectly after a very long time, probably in consequence of a molecular alteration of the inulin. (Dubrunfaut.)—The aqueous solution of inulin is transparent; gummy if it contains 1 pt. inulin to  $\frac{1}{2}$  pt. water, but not pasty (Gaultier); the solution of 1 pt. inulin in 4 pts. water is less gummy than an equally strong solution of gum-arabic; it may be filtered, does not froth when agitated, but if cooled deposits nearly all the inulin in the crystalline form after a few hours (Rose); after 48 hours it solidifies to a white, opaque, curdy mass, which cannot be poured out. (Braconnot.) A solution of 1 pt. inulin in 17 pts. water at  $15^{\circ}$  does not deposit any thing after 48 hours. (Payen, John.)—A concentrated solution of inulin in boiling water deposits transparent inulin on cooling, sometimes in crystalline aggregates; the solution saturated at  $175^{\circ}$  deposits on cooling aggregates of spherules and plates. (Payen.)—A concentrated solution of inulin becomes covered with a film on evaporation, and solidifies to a granular mass on cooling. (Payen.)

2. With *iodine*, inulin obtained from elecampane-root forms a greenish yellow compound which in time loses nearly all its iodine, becoming pale yellow, and is decomposed by boiling water. (Gaultier.)—3. *Chlorine* does not precipitate aqueous inulin. (Payen.)—4. Inulin dissolves with brown colour in *oil of vitriol*; the solution is precipitated by ammonia, not by water or alcohol. (Gaultier.)—5. It is not soluble in *hydrochloric acid* (Gaultier); dissolves in *dilute hydrochloric acid* (Biltz). For the decomposition of inulin by dilute and concentrated acids, see page 115.

*With Bases*.—Inulin absorbs 3.29 p. c. *ammonia*. (Mulder.)—It dissolves in cold aqueous *potash*, forming a colourless solution which leaves, on evaporation, a nearly colourless gum, and when mixed with acids deposits after a while unaltered inulin.

*Inulin-baryta*.—Produced by adding hydrate of baryta or chloride of barium mixed with potash to an aqueous solution of inulin. White curdy flocks, which gradually cake into a soft viscid mass. The warm aqueous solution, when left to evaporate, becomes covered with yellow crystalline fibres. By repeated solution in water and evaporation of the solution, the compound deposits carbonate of baryta and becomes soluble in cold water. (Payen.)—Inulin-baryta dissolves easily in nitric, with difficulty in hydrochloric acid (Gaultier); also in glacial acetic acid, and in excess of aqueous inulin. (Payen.)

Aqueous-inulin does not precipitate *strontia-water*, *lime-water*, *aluminate of potash*, or *silicate of potash*. (Gaultier.)

*Inulin with Lead-oxide*.—Aqueous inulin added to aqueous neutral acetate of lead mixed with ammonia, throws down a bulky compound (flocculent according to Croockwit) of inulin and oxide of lead (Parnell), which must be pressed in air free from carbonic acid, and dried, first over oil of vitriol and sticks of potash, then for some hours at  $100^{\circ}$  (Croockwit.)—Aqueous inulin does not precipitate aqueous *acetate of lead* either *neutral* or *basic* (Parnell); at the boiling heat it dissolves 26.7 p. c. lead-oxide in a few minutes, but is decomposed by half-an-hour's boiling therewith. (Mulder.)—The compound of inulin and lead-oxide dried at mean temperature, is white, pulverulent, partially

deliquescent at  $100^{\circ}$ , and varies in composition even when prepared under similar circumstances (Parnell), because, by the action of the base, the inulin is partly converted into sugar, and the sugar into glucic acid. (Löwig, *Org. Verb.* 1, 363.) Inulin from dahlia-tubers and inulin from elecampane-roots form different compounds with oxide of lead; and even with the same kind of inulin, different compounds, enclosing various quantities of glucate of lead, are obtained, according to the quantities of ammonia and acetate of lead added. (Crookwit.)

				Parnell.		Croockwit.				
				<i>a</i>		<i>b</i>		<i>c</i>		
Calculation, according to Parnell.				from Dahlia-tubers.		from Elecampane-roots.		from Dahlia-tubers.		
				at 100°						
24 C .....	144.0	....	22.46	....	22.46	.....	21.52	.....	25.20	
18 H .....	18.0	....	2.79	....	2.94	.....	2.85	.....	3.32	
18 O .....	144.0	....	22.46	....	23.37	.....	22.56	.....	27.56	
3 PbO .....	335.4	....	52.29	....	51.23	.....	53.07	.....	43.92	
<hr/>										
C <sup>24</sup> H <sup>18</sup> O <sup>18</sup> ,3PbO	....	641.4	....	100.00	....	100.00	.....	100.00	.....	100.00

				Parnell.		Croockwit.				
				<i>d</i>		<i>e</i>		<i>f</i>		
				from Dahlia-tubers.		from Elecampane-roots.		from Dahlia-tubers.		
				at 100°						
24 C .....	144	....	16.14	....	16.65	.....	19.13	.....	17.38	
21 H .....	21	....	2.35	....	2.44	.....	2.39	.....	2.16	
21 O .....	168	....	18.83	....	18.48	.....	20.61	.....	18.32	
5 PbO .....	559	....	62.68	....	62.43	.....	57.87	.....	62.14	
<hr/>										
C <sup>24</sup> H <sup>21</sup> O <sup>21</sup> ,5PbO	.....	892	....	100.00	....	100.00	.....	100.00	.....	100.00

*a* contains, in the air-dried state, 7 p. c. water, *d*, 2 p. c. water, which is given off at  $100^{\circ}$ .

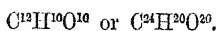
Aqueous solutions of *ferrous sulphate*, *ferric sulphate*, *cupric sulphate*, *mercuric nitrate*, *nitrate of silver*, and *chloride of gold*, are not precipitated by aqueous inulin. (Payen.)—Inulin is dissolved by aqueous *cuprammonia*, without previous tumefaction (Cramer, *J. pr. Chem.* 73, 16); the solution yields after a few hours, a copious blue amorphous precipitate insoluble in water and ammonia, soluble in tartaric and nitric acids. (Schlossberger, *J. pr. Chem.* 73, 373.)—Inulin dissolves gradually in aqueous *nickel-ammonia*. (Schlossberger, *J. pr. Chem.* 73, 370.)

Inulin dissolves in warm, but not in cold *glacial acetic acid* (Biltz.)

*Infusion of galls* throws down from aqueous inulin a white somewhat elastic precipitate (Gaultier), which redissolves below  $100^{\circ}$  (Pelletier & Caventou); it is not produced till after the lapse of 6 hours, has a pearly lustre, dissolves in water at  $50^{\circ}$  (Payen), and, according to Braconnot, consists of inulin free from tannin.

Inulin is insoluble in *alcohol*. (Rose.) Inulin from morel is insoluble in absolute alcohol and in *ether*, but dissolves in 100 pts. of 80 p. c. alcohol, and in a smaller quantity of 40 p. c. alcohol.

## Lichenin.



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 GUÉRIN-VARRY. *Ann. Chim. Phys.* 56, 247; *J. pr. Chem.* 3, 346; abstr. *Ann. Pharm.* 13, 71.  
 MULDER. *Natuur en Scheikundig Archief*, 1837, No. 4.—*Bull. de Néerland*, 1838, 41; abstr. *J. pr. Chem.* 15, 299; *Ann. Pharm.* 28, 279.  
 PAYEN. *N. Ann. Sc. nat. Bot.* 14, 85.—*Inst.* 206, 128, and 145.  
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 VOGEL. *Linnæa*, 15, 59; abstr. *J. pr. Chem.* 25, 382.  
 DAVIDSON. *Ed. N. Phil. J.* 28, 260; *J. pr. Chem.* 20, 354.  
 KNOP & SCHNEIDERMAN. *J. pr. Chem.* 40, 389. *Ann. Pharm.* 55, 164,

*Lichen-starch, Flechtenstärkmehl, Moostärkmehl, Lichénine* (Guérin).—Formerly classed amongst the different kinds of vegetable mucus, but included by Berzelius among the starches.

*Sources.*—In lichens and mosses, especially in *Cetraria islandica*, *C. glauca*, *Ramelina fraxinea*, *R. fastigiata*, *Ulna barbata*, *U. plicata* (Berzelius); in *Parmelia parietina*, *P. saxatilis*, *Peltigera canina*, *Cladonia rangiferina*, *C. pyxidata*, *Evernia furfuracea* and *Delesserea pinnata*; in worm-moss (the produce of about 12 species of algæ) (Schmidt, *Ann. Pharm.* 51, 58); in *Sticta pulmonacea* and others.—*Cetraria islandica* contains inulin and starch as well as lichenin, the starch not occurring in granules, but forming an integral part of the cellular membrane, which consists of cellulose (Payen).—Lichenin does not occur in isolated granules, like starch, but as a smaller mass uniformly distributed amongst the cells (Knop & Schnedermann).—According to Maschke *J. pr. Chem.* 61, 1), it is formed from starch by the action of the free acid in the *Cetraria islandica*, and is identical with his soluble starch. (pp. 82, 86.)

*Preparation.* 1. Iceland moss is freed from the bitter principle contained in it, by a process given below; it is then boiled for two hours with 9 pts. of water, strained boiling hot, pressed, and left to cool. The jelly which separates on cooling is freed from water by hanging it up in a linen cloth, or letting it lie on blotting paper. (Berzelius.) After this treatment it is still black, but is obtained colourless by dissolving it in boiling water and precipitating the filtrate with alcohol. (Guérin-Varry.)

Berzelius removes the bitter matter of Iceland moss by macerating 1lb. of the lichen for 24 hours with 18lbs. water and  $\frac{1}{8}$ lb. potash, and repeatedly washing it with water, without pressure. Payen washes successively with ether, alcohol of sp. gr. 0.83 and 0.90, cold water, very weak solution of carbonate of soda, aqueous hydrochloric acid of the strength of 1 per cent., and lastly, with pure water.—Davidson macerates 112lbs. of Iceland moss for 14 days with potash-ley prepared from 4lbs. of potash, or for 6 days with milk of lime prepared from 6lbs.

of lime, then washes with dilute sulphuric acid, and finally with water. Chloride of lime may also be used for the maceration.

2. A large quantity of hydrochloric acid is poured upon Iceland moss, and the clear solution obtained after diluting and straining, is precipitated with alcohol. The precipitated lichenin may be freed from water, and rendered friable by repeated treatment with absolute alcohol, and then freed from adhering hydrochloric acid by immersion in running water. (Knop & Schnedermann.)

In this process, according to K. & S., two modifications of lichenin may be produced.—*a*. If the mucilage prepared with fuming hydrochloric acid, and diluted, be mixed with alcohol till turbidity ensues, then with a little more alcohol, so that part of the lichenin and all the dirt may be thereby precipitated, then afterwards carefully strained, the liquid if necessary being poured back,—a clear solution is obtained from which alcohol throws down white flocks. These flocks dried on a hair sieve, yield a colourless transparent mass, undistinguishable from common starch which has been boiled and dried again.—*b*. When the hydrochloric acid extract is immediately precipitated with alcohol, washed with aqueous alcohol, and boiled, a substance is separated by filtration which is no longer coloured blue by iodine, and exhibits the characters of Mulder's lichenin.

In a later communication, Knop and Schnedermann make the following statement:—Lichenin prepared by *b* swells up in water to a slippery mass, which is coloured by iodine. If it be boiled with water, neither the clear solution nor the jelly which forms on cooling, is coloured blue by iodine; but on precipitating with alcohol, the lichenin, freed from alcohol by washing with water, is again coloured blue by iodine.

*Properties.* Colourless (Payen) or yellowish, hard, brittle, translucent mass, vitreous on the fractured surface. Difficult to pulverize.—Nearly inodorous; tasteless. Permanent in the air.

				Mulder.		Knop & Schnedermann.	
24 C .....	144 .....	44.44 .....	44.29 .....	44.4			
20 H .....	20 .....	6.17 .....	6.28 .....	6.0			
20 O .....	160 .....	49.39 .....	49.43 .....	49.6			
$C^{10}H^{10}O^{10}$ .....				324 .....	100.00 .....	100.00 .....	100.00

Knop & Schnedermann's lichenin was turned blue by iodine.

According to Guérin-Varry, lichenin is  $C^{10}H^{10}O^{10}$ ; see his analysis (*Ann. Chim. Phys.* 56, 245); according to Vogel, it resembles amyloid, inasmuch as, like that substance, it forms the cell-walls of lichens.

*Decompositions.* 1. Lichenin yields by *dry distillation* products doubtless similar to those obtained from starch. It yields carbonic acid, carbonic oxide, a small quantity of carburetted hydrogen, aqueous empyreumatic acetic acid, and a brown oil, but no ammonia, and leaves  $\frac{1}{2}$  charcoal. (Berzelius).—According to Proust, traces of ammonia are likewise obtained.—2. The aqueous solution of lichenin slowly turns mouldy on exposure to the *air*, but without acquiring any bad taste or smell. (Berzelius).—It turns sour in a few days. (Guérin).—3. By continued *boiling* of its aqueous solution, it partly loses the property of separating on cooling. (Berzelius).—4. By boiling with very dilute *sulphuric acid*, it is partly converted into sugar.

(Kirchhoff, *Schw.* 14, 388). 100 pts. treated with 250 pts. oil of vitriol yield 53.91 pts. anhydrous sugar.—5. *Chlorine gas* passed into the solution removes any accidental brown colour, without producing further decomposition. (Berzelius.)—6. Gently heated *nitric acid* dissolves lichenin with facility, producing a non-mucilaginous fluid, while, at a higher temperature, oxalic acid is formed, but neither mucic acid, nor stearin. (Berzelius, Proust.) 100 pts. lichenin set aside for a month, at a temperature of 20° to 25° in contact with 600 pts. nitric acid of sp. gr. 1.84, yield saccharic acid, and at 40° a much larger quantity. If the liquid be heated to 60°, it yields on cooling crystals of oxalic acid, 100 pts. lichenin producing 48.17 pts. of the hypothetical anhydrous acid. (Guérin.)

*Combinations.*—Lichenin immersed in cold water slowly swells up to a considerable mass, but without perceptibly dissolving. In boiling water, it dissolves completely to a thick gum. The concentrated solution solidifies to a jelly on cooling. (Guérin-Varry.) The solution, if left to evaporate, becomes covered with films soluble in water. (Guérin, Berzelius.) The jelly gradually contracts on standing, so that the supernatant water still retains a little lichenin in solution, becomes covered with a crust if longer boiled, and ultimately loses the power of gelatinising on cooling (Berzelius); it is thereby converted into a gummy mass. (John.)—*Iodine* colours lichenin greenish-brown, according to Berzelius; blue, according to Guérin-Varry, but much less deeply than starch; yellow, according to Mulder, or green from admixture of starch. (*Comp.* Knop & Schnedermann, p. 120). The green solution of iodine in lichenin set aside in open vessels for 24 hours, deposits lichenin, leaving iodide of starch in solution. (Mulder.)—The decoctions of *Cetraria islandica* and *Parmelia parietina* acquire a fine blue colour when treated with alcoholic tincture of iodine, that of *Sticta pulmonacea* becomes bluish-green; all these decoctions are decolourised by boiling; but that of the first-mentioned lichen recovers its blue colour on cooling. (Mulder.)

In fuming hydrochloric acid, lichenin swells up to a jelly as transparent as glass, from which alcohol precipitates unaltered lichenin. (Knop & Schnedermann.)

Lichenin absorbs 2.66 p. c. ammonia gas, but gives it up completely at 100°. (Mulder.)

With aqueous potash it forms a pale yellow, perfectly mobile solution not precipitable by acids. (Berzelius.)—The films which collect on the surface of aqueous lichenin while boiling, are rendered ductile, like turpentine, by immersion in aqueous potash. (John.)

Lichenin dissolves in hot aqueous carbonate of potash, also in hot baryta- and lime-water. (Berzelius.)

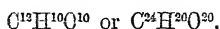
*Lead-compound of Lichenin.* Basic acetate of lead is dropped into hot aqueous lichenin, and the product is washed and dried.—White precipitate containing 55.26 p. c. oxide of lead ( $C^{24}H^{20}O^{20}$ ,  $4PbO = 57.9$  p. c.  $PbO$ ). (Mulder). It dissolves in acetic acid (Guérin). Aqueous lichenin from *Ramelina fraxinea* is not precipitated by basic acetate of lead. (Berzelius.)

Lichenin is rendered slightly turbid by mercurous nitrate; not precipitated by acetate of alumina or ferrous sulphate.

*Infusion of galls* produces a precipitate in the aqueous solution of lichenin from *Ramelina fastigiata* or *R. fraxinea*. (Mulder, *Phys. Chem.* 225.)

Lichenin is insoluble in alcohol and in ether.

## Paramylone.



GOTTLIEB. *Ann. Pharm.* 75, 51; *Pharm. Centr.* 1850, 856.

In *Euglena viridis*, a green infusorium living in water.

Fresh *Euglenæ*, mechanically freed from adhering vegetable matter, sand, &c., are exhausted successively with ether, 80 p. c. alcohol, and boiling alcoholic hydrochloric acid, to remove fat, colouring matter, and nitrogenous substance, whereby the envelopes of most of the animalcules are lacerated, and granular paramylone is set free. From the resulting mixture of paramylone envelopes, and uninjured animalcules, the two latter are for the most part removed by repeated stirring with water and straining; the water which runs through then depositing paramylone in a purer state. Paramylone thus prepared still retains about 1.4 p. c. ash and membranes, which may be removed by dissolving it in weak potash-ley, precipitating the filtrate with hydrochloric acid, and washing out the jelly. In the course of the preparation a brown substance is formed by the action of the potash on the admixed membranes: it may be removed by repeatedly dissolving the paramylone in potash-ley and precipitating with hydrochloric acid.

*Properties.* White granules, which are smaller than those of wheat-starch; and give off their adhering water at  $100^{\circ}$ .—After precipitation from the potash-solution by hydrochloric acid, and drying, it forms irregular, pale yellow, translucent, tenacious, scarcely friable lumps, which do not give off their adhering water below  $110^{\circ}$ .

						Gottlieb.	
						a.	b.
						at $100^{\circ}$	at $110^{\circ}$
24 C.....	144	....	44.44	.....	44.87	....	44.22
20 H .....	20	....	6.17	.....	6.37	....	6.30
20 O .....	160	....	49.39	.....	48.76	....	49.48
<hr/>						<hr/>	
$C^{24}H^{20}O^{20}$ .....	324	....	100.00	....	100.00	....	100.00

a, after deducting 1.4 p. c. ash; b paramylone purified with potash-ley. The compound is nearly related to cellulose. (Gottlieb.)

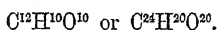
*Decompositions.* 1. Melts when heated, and burns with an odour of sugar, leaving an easily combustible charcoal.—In air heated to  $200^{\circ}$  it does not melt, but turns brown and then yields to water, a tasteless gum, insoluble in alcohol.—2. With *nitric acid* it yields a large quantity of oxalic acid.—3. It is not altered by hot *dilute acids*; by boiling for six days with *dilute sulphuric acid*, it is partly converted into a brown, greasy mass, which decomposes aqueous potassio-cupric tartrate only at the boiling heat, with separation of cuprous oxide.—4. Boiled with *strong hydrochloric acid*, it dissolves to a brown syrup containing fermentable sugar, capable of reducing potassio-cupric tartrate.—Paramylone is not converted into sugar by *diastase*.

*Combinations.* Paramylone is insoluble in *water*. — That which has been precipitated by acids swells up in water, but without gelatinising. — It is not coloured by *iodine*.

Paramylone does not dissolve in *dilute acids*, or in *aqueous ammonia*, either cold or at the boiling heat. — It dissolves without decomposition in strong *potash-ley*, and is precipitated therefrom by carbonic acid almost in the pure state; by acidulated alcohol in white flocks; by absolute alcohol in combination with a small quantity of carbonic acid and potash. The last precipitate dries up to a yellow, translucent mass, and gives up potash when washed with alcohol.

Paramylone is not altered by *saline solutions*, and is insoluble in *alcohol* and *ether*.

### Cellulose.



- FOURCROY. *Système des Connaissances chimiques*, 8, 87.  
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 SAUSSURE. *A. Gekl.* 4, 681.  
 RUMFORD. *Schw.* 8, 160.  
 BRACONNOT. *Ann. Chim. Phys.* 12, 172; *Schw.* 27, 328; *Gilb.* 63, 347.  
 READE. *L. Ed. Mag. J.* 11, 421.  
 SCHLEIDEN. *Wieg. Arch.* 1838, 59; *Pogg.* 43, 391. — *Ann. Pharm.* 42, 298. — *Grundz. d. wissensch. Botanik*, Leipzig, 1849, 1, 172.  
 LIEBIG. *Ann. Pharm.* 17, 139. — 30, 266. — 42, 306.  
 PAYEN. *N. Ann. Sc. nat. Bot.* 11, 21 and 27. — 14, 37. — *Compt. rend.* 18, 271. — *Compt. rend.* 48, 210 and 275; *N. J. Pharm.* 35, 88 and 185; abstr. *Rép. Chim. pure*, 1, 270. — *Compt. rend.* 48, 319, 326, 328, 358 and 362. — *Compt. rend.* 48, 772 and 893; abstr. *Rép. Chim. pure*, 1, 359 and 434.  
 F. L. WINCKLER. *J. pr. Chem.* 17, 65.  
 HERMANN. *J. pr. Chem.* 23, 380; 27, 165.  
 FROMBERG. *Scheik. Onderzoek.* 2, 36; abstr. *Ann. Pharm.* 48, 353; *J. pr. Chem.* 32, 198.  
 V. BAUMHAUER. *Scheik. Onderzoek.* 2, 62 and 194; abstr. *Ann. Pharm.* 48, 356; *J. pr. Chem.* 32, 204 and 210; *N. Br. Arch.* 53, 68.  
 MULDER. *Scheik. Onderzoek.* 2, 76; abstr. *J. pr. Chem.* 32, 336. — *J. pr. Chem.* 39, 150.  
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 ROCHLEDER & HELDT. *Ann. Pharm.* 48, 8.  
 SCHAFFNER. *Ann. Pharm.* 50, 148.  
 ROCHLEDER. *Ann. Pharm.* 50, 225.  
 REINSCH. *Jahrb. pr. Pharm.* 14, 25.  
 POUMARÉDE & FIGUIER. *Mémoire sur le Ligneux, etc.*, Paris, 1847; *N. J. Pharm.* 12, 81; *J. pr. Chem.* 42, 25.  
 CHODNEW. *Ann. Pharm.* 51, 393.  
 MITSCHERLICH. *Berl. Akad. Ber.* 1850, 102; *Ann. Pharm.* 75, 305; *J. pr. Chem.* 50, 144.  
 F. SCHULZE. *Beiträge zur Kenntniss des Lignins*, Rostock, 1856; abstr. *Chem. Centr.* 1857, 321.



- SCHWEIZER. *Chem. Centr.* 1858, 49; *J. pr. Chem.* 72, 1095.—*J. pr. Chem.* 78, 370; *Rép. Chim. pure*, 2, 142.
- CRAMER. *J. pr. Chem.* 73, 1; *Chem. Centr.* 1858, 50; abstr. *Compt. rend.* 48, 270.
- SCHLOSSBERGER. *Ann. Pharm.* 107, 22; *J. pr. Chem.* 73, 370; *N. Br. Arch.* 95, 145.—*Ann. Pharm.* 110, 246; *N. Jahrb. Pharm.* 12, 6; abstr. *J. pr. Chem.* 77, 508; *Rép. Chim. pure*, 1, 432.
- ERDMANN & MITTENZWEY. *J. pr. Chem.* 76, 386; *Chem. Centr.* 1859, 642.
- FRÉMY. *Compt. rend.* 48, 202; *N. J. Pharm.* 35, 81; abstr. *Rép. Chim. pure*, 1, 269.—*Compt. rend.* 48, 325 and 360.—*Compt. rend.* 48, 667 and 862; *N. J. Pharm.* 35, 321 and 401; abstr. *Inst.* 1859, 121 and 151; *Rép. Chim. pure*, 1, 357 and 433; *Pharm. Vierteljahr.* 9, 221.—*N. J. Pharm. Inst.* 1859, 357; *Rép. Chim. pure*, 1, 602; *Chem. Centr.* 1860, 4.
- PELOUZE. *Compt. rend.* 48, 210 and 327; *N. J. Pharm.* 35, 209; *Inst.* 1859; *Rép. Chim. pure*, 1, 272; *Dingl.* 151, 394.

*Specially relating to Pollenin.*

- JOHN. *Chem. Schriften*, 5, 39; *Schw.* 12, 144.
- BUCHHOLZ. *A. Gehl.* 6, 573.
- FRITZSCHE. *Pogg.* 32, 481.
- BRACONNOT. *Ann. Chim. Phys.* 42, 98; *N. Tr.* 21, 164.
- HERAPATH. *Chem. Soc. Qu. J.* 1, 1.
- MUSPRATT. *Ann. Pharm.* 51, 280.

*Specially relating to Fungin.*

- BRACONNOT. *Ann. Chim.* 79, 276.
- VAUQUELIN. *Schw.* 12, 253.
- SCHRAEDER. *Schw.* 33, 410.
- PAYEN. *N. Ann.-Sc. nat. Bot.* 14, 89.
- SCHLOSSBERGER & DÖPPING. *Ann. Pharm.* 52, 113.

*Woody Fibre, Lignin, Zellstoff, Pflanzen-zellstoff, Faser, Holzfaser, Pflanzenfaser, Pflanzenfaserstoff, Ligneux.*

Payen and others make a distinction, between cellulose or woody fibre properly so-called, and the encrusting matter (Turpin's *sclerogen*, Schulze's *lignin*) which they regard as a peculiar constituent of the cellular tissue. This encrusting matter has not however been isolated, and Schleiden (*Grundzüge d. wissenschaft. Bot.* Leipzig, 1849, 1, 173) contests its existence as a distinct compound. The encrusting matter treated successively with potash and iodine, assumes an orange-yellow colour, and is thereby distinguished from cellulose, which turns blue under the same circumstances. (Payen, *N. Ann. Sc. nat. Bot.* 13, 305.) Schulze's lignin dissolves in a mixture of chlorate of potash and nitric acid, in oil of vitriol, and in a concentrated aqueous solution of chloride of zinc (*comp.* Payen, *N. Ann. Sc. nat. Bot.* 11, 27; abstr. *Compt. rend.* 81, 51; *J. pr. Chem.* 16, 436.—v. Baumbauer, *Scheik. Onderzoek.* 2, 62; *J. pr. Chem.* 32, 204; *Repert.* 95, 220.—F. Schulze, *Beiträge zur Kenntniss des Lignins*, Rostock, 1856; abstr. *Chem. Centr.* 1857, 321).

The substances formerly distinguished as *Pollenin*, *Fungin* or *Medullin*, appear to be nothing but cellulose in various degrees of purity. A few other substances allied to cellulose are treated in an Appendix.

*Sources.* 1. *In the Vegetable Kingdom.*—Cellulose forms the principal part of the cellular tissue of plants. It is indispensably necessary for the formation and development of the cells (Schleiden);

it is the plastic material, not only of the primary cell-wall, but likewise of all the spiral or otherwise formed deposits which attach themselves to its inner surface as the plant grows, and appear to partake of the structure of the cell-wall itself. (Scheiden, Schulze.) Cellulose is found in its purest state in the walls of young vegetable cells, as in the spongioles of the rootlets, the younger organs of the leaf and flower, the fleshy structures of certain fruits, &c.; more frequently, however, it is found associated or combined with foreign matters, especially in the cell-walls of older plants, in the wood, &c. Such foreign admixtures, produced as the growth of the plant advances, and often very intimately united with the cellulose are: colouring matters, fats, resins, gum, mucus, starch, sugar, and salts, both organic and inorganic. According to Payen, cellulose, even in the youngest parts of plants, is united with a nitrogenous substance, resembling protein. On Payen's *matière incrustante*, see page 124.

Frémy (*Compt. rend.* 48, 202) is of opinion that the cell-walls of plants consist, not of one, but of several substances, because he finds that cuprammonia (see *Combinations*, p. 142) dissolves only the outer wall of many vegetable cells, forming a solution from which pure cellulose may be separated by water, and leaving an inner membrane (coloured green by the re-agent and yielding pectic acid when treated with acids), whereas other plant-cells are not attacked by aqueous cuprammonia. He likewise admits the existence of various kinds of cellulose, whose different behaviour towards solvents is not determined by their different degrees of cohesion, inasmuch as the solubility of cellulose in aqueous cuprammonia is not in proportion to its cohesive power. Nevertheless, Payen (*Compt. rend.* 48, 210) is of opinion that the different chemical relations of vegetable cellular membranes are determined by admixtures of organic and inorganic substances, as well as by their different degrees of cohesion, which latter cannot be measured solely by the hardness of the different substances composed of cellulose or woody fibre. Thus, according to his observations (*Compt. rend.* 48, 319), the cellulose in the pith of the stem of herbaceous and woody plants, both above and below the surface of the soil, does not differ greatly from that which constitutes cotton and other fibres used for spinning, and the cell-walls of the various kinds of vegetable tissue. But after Pelouze (*Compt. rend.* 48, 210 and 327) had observed that cellulose which has been dissolved in aqueous cuprammonia and precipitated by hydrochloric acid, is much more soluble in hydrochloric acid than natural cellulose,—and that cellulose treated with melting potash at 150°—190° becomes much more soluble in weak aqueous potash,—and had thence concluded that the latter kind of cellulose is a modification of that which occurs naturally, Payen (*Compt. rend.* 48, 358) likewise recognised the existence of different isomeric modifications of cellulose, although he still maintained that the skeleton of plants, the walls of the cells, fibres, and vessels in general, consist of *one and the same* kind of cellulose, and that the various conditions of cellulose in plants are determined essentially by their state of aggregation or by the presence of foreign bodies.—Frémy on the other hand maintains (*Compt. rend.* 48, 67) that the different modifications of cellulose cannot arise from the admixture of foreign substances, inorganic compounds, for example, inasmuch as the solubility of cellulose in cuprammonia may vary, although the amount of inorganic matter associated with it remains constant;

thus the insoluble pith of plants is rendered soluble by many hours heating to about  $150^{\circ}$  or by prolonged boiling. As isomeric modifications of natural cellulose, he distinguishes: 1. That part of the vegetable tissue which is soluble in aqueous cuprammonia,—the true cellulose or woody fibre;—2. The part which is insoluble in aqueous cuprammonia, but is rendered soluble by treatment with certain chemical re-agents: *Paracellulose*. The latter is found in nature associated with true cellulose, constituting the utricular tissue of the medullary rays. As two further modifications, Frémy distinguishes *Vasculose*, which forms the vascular tissue, and *Fibrose*, which forms the woody tissue, both of which differ in some respects from true cellulose. (*vid. inf.*)

Cellulose occurs tolerably pure in the fibre of cotton, flax, and hemp, therefore in bleached linen; in the byssus used for wrapping mummies (Thomson, *Ann. Pharm.* 69, 128); in white (Swedish) paper.—It occurs pure (not pure, according to v. Baumhauer) in the pericarp of *Phytalephas* (Payen); is contained, to the amount of 12 per cent. in the manna of *Eucalyptus dumosa* (Anderson, *N. Ed. Phil. J.* 47, 132; *J. pr. Chem.* 47, 449); it forms the envelopes of starch-granules (Melsens); the membranes which enclose the granules of starch-granules (Nägeli, *Die Stärkmehlkörner*, 1858); it is a constituent of lignite and coal (Schulze, *Lieb. Kopp. Jahresber.* 1855, 702 and 1019).

As *Pollenin*. In the pollen of flowers: of tulips (John), of date-flowers (Fourcroy & Vauquelin, *A. Gehl.* 1, 507), of lilies and of *Cactus speciosissimus* (Herapath), in the seeds of lycopodium (Buchholz, *A. Gehl.* 6, 573).—As *medullin*, in the pith of plants, especially of sunflowers and of the elder-tree (John, *Chem. Schriften*, 4, 204).—As *Fungin* in fungi, as *Agaricus volcracius*, *A. piperatus* and *A. stypticus*, *Boletus juglandis*, and *B. pseudo-igniacarius*, *Phallus impudicus*, *Merulius Cantharellus*, *Hydnum repandum* and *H. hybridum*, *Mucor septicus*, (Braconnot, *Ann. Chim.* 79, 276); *Agaricus campestris*, *A. bulbosus*, *A. theogalus*, *A. muscarius* (Vauquelin, *Schw.* 12, 253); *Helvella mitra* (Schrader, *Schw.* 33, 410).—As *Lichenin* in the skeleton of lichens (p. 119).—The cellulose of Iceland moss appears to be in a state of transition between true cellulose and starch (Fromberg).—As *cork cellulose*: existing in an impure state in cork, the outer bark of the cork-oak.

2. *In the Animal Kingdom*.—Degenerated human spleen and some parts of the human brain contain a substance resembling cellulose (Virchow, *Compt. rend.* 37, 492 and 860).—In the skin of silk-worms, probably also in the wing-cases of cantharides, the shells of crabs and lobsters (Peligot, *Compt. rend.* 47, 1037; *Rép. Chim. pure*, 1, 234); not in the wing-cases of cockchafer or in the carapaces of craw-fish and shrimps, therefore also probably not in the skin of the silk-worm (Städeler, *Ann. Pharm.* 111, 28). see *Tunicin*.

On the formation of cellulose in plants, see Schleiden, also Rosignon (*Compt. rend.* 14, 873). On the detection and estimation of cellulose, see Poggiale (*N. J. Pharm.* 36, 121).

*Preparation*. A portion of a plant containing cellulose as nearly pure as possible—such as cotton, flax-fibre, hemp-fibre, pith, &c., is exhausted successively with water, alcohol, ether, hydrochloric acid, and aqueous alkali, then perhaps treated with chlorine, and dried after thorough washing.

1. Payen boils finely pulverized oak-, beech-, or acacia-wood to dryness with potash-ley three times in succession; washes with water, hydrochloric acid, ether, and alcohol; boils with water; treats the remaining substance repeatedly with aqueous ammonia, potash, hydrochloric acid, and water in succession, sometimes also suspends it in water and treats it with chlorine; and finally washes it with alcohol and ether.— Or he exhausts finely divided fir-wood with water, alcohol, ether, acids, and weak soda-ley, then with hot concentrated soda-ley, afterwards with hydrochloric acid and water; triturates the woody-fibre on a grindstone; treats it, suspended in water, with chlorine gas; and lastly with aqueous potash, hydrochloric acid, and water in succession. The perisperm of *Phytalephas* exhausted successively with aqueous ammonia, water, alcohol, ether, then again with alcohol, ammonia, glacial acetic acid and water, yields pure cellulose. (Payen.)

2. Spiral vessels of *Agave americana*, elder-pith, or the pith of *Phytolacca decandra* are exhausted with glacial acetic acid, water, alcohol, and ether successively, or with one or more of these re-agents (Mulder). White cotton is boiled for half-an-hour with dilute sulphuric acid, then for a while with strong potash-ley, afterwards washed with water, alcohol, ether-alcohol, and finally with boiling water. (Blondeau de Carolles.)

3. Dried parts of plants, such as *Agaricus albus*, turnips or white cabbage, or Iceland moss previously exhausted for several days with weak soda-ley, are boiled with water, till the decoction is no longer coloured by alcoholic iodine, and runs off nearly colourless; the residue is repeatedly digested with soda-ley of 10 per cent., till the extract is no longer precipitated by hydrochloric acid; and the residue, after being washed with water and pressed, is successively digested with alcohol heated to 30°, repeatedly with ether and with dilute hydrochloric acid (1 : 21), and finally exhausted with water and alcohol. (Fromberg.)

4. Finely comminuted parts of plants containing woody fibre are macerated four times in succession for seven days each with cold potash-ley, the residue being each time washed for a long while with water and glacial acetic acid, and finally well boiled with water, alcohol, and ether. (v. Baumhauer.)

5. One part of vegetable tissue is macerated for fourteen days at a temperature of about 115° in a mixture of 12 pts. nitric acid of sp. gr. 1.160 and 18 pts. chlorate of potash—cellulose being then taken up into the solution, and the residue is washed with water and with alcohol. (Schulze.) Cellulose thus prepared is contaminated with considerable quantities of a chlorinated substance produced by the action of chlorine on the woody fibre. (Ritter, *Private communication*.)

6. The pith of elder-stems, burdock-roots or sunflower-stalks gathered in August and comminuted, is exhausted successively with water, alcohol, and ether, then with weak potash-ley, and washed with water. (Schaffner.)

The following plants and parts of plants also finally leave cellulose when treated as follows:

7. Finely pulverized coffee-beans are exhausted as completely as

possible with ether, alcohol, water, boiling weak potash-ley, boiling dilute hydrochloric acid, and water; the residue rubbed up to a pulp with water is left to itself till white flocculent cellulose has settled down, and this deposit is dried and exhausted with absolute alcohol. (Rochleder.)—8. Lichens are exhausted with cold water, alcohol, aqueous ammonia, glacial acetic acid, and ether, and lastly boiled with water (Payen); they are exhausted with alcoholic ammonia, weak alcohol, ether, alcoholic potash, boiling aqueous potash, a large quantity of water, boiling weak hydrochloric acid, and boiling water. (Rochleder & Heldt.) They are steeped for four to six days in concentrated hydrochloric acid renewed every day, and the residue is repeatedly exhausted by successive treatment with alcoholic ammonia and hydrochloric acid, which however does not completely remove a brown substance formed from the cetraric acid. (Kopp & Schnedermann.)—9. Pressed, dried, and finely comminuted *Conferva* are exhausted with alcohol, aqueous ammonia, dilute soda, and potash-ley, and the residue suspended in water is treated with chlorine, and afterwards washed with weak hydrochloric acid, water, ether and alcohol. (Payen.)—10. Fungi, after being pressed, are exhausted with water, alcohol, and weak aqueous potash (Braconnot), or reduced to dry powder, and treated successively with ether, alcohol, hot ammonia, hydrochloric acid, and weak aqueous potash, continually washed in the intervals with water, then diffused in water and treated with chlorine, and finally again treated with alcohol and ether. (Payen.)—11. The pollen of tulips is exhausted successively with water, alcohol, and aqueous potash. (John, Buchholz.)—12. Rasped cork is exhausted with alcohol, boiled with 8 pts. nitric acid, of sp. gr. 1.30, till the suberin is dissolved and the wax has separated as an oily layer, and the cellulose diffused in flocks through the acid liquid, is repeatedly washed with alcohol. (Schlossberger & Döpping, *Ann. Pharm.* 52, 113.)

*Properties.* In the moist state colourless and translucent; in the dry state, white, and nearly translucent. Different in appearance according to the tissues from which it has been obtained, it either exhibits the original structure of the vegetable tissue, or consists of a network of fibres more or less united with one another.

Closely aggregated cellulose is obtained from ebony-, guaiac-, and oak-wood, from the pericarp of vegetable ivory (*Phytelphas*), from nuts, from nodes of grass-stems, &c.; loosely united cellulose is yielded by cedar-, pine-, and birch-wood, the stems of grasses, herbs, &c. Very easily separable, and at the same time very long, tough, and flexible, are the fibres of flax, hemp, New Zealand flax (*Phormium tenax*), and cocoa-nut, the spiral vessels of the pisang, &c.; completely separated very flexible and tough, are the fibres of cotton and of seed-wool in general.

Cellulose, separated from its solution in aqueous cuprammonia, forms loose flocks, which dry up to grey, horny lumps translucent on the edges (Schweizer, Schlossberger); after precipitation with alcohol, it forms white threads, which crumble to a white powder when washed with hydrochloric acid (Erdmann).—Sp. gr. of woody fibre 1.25 to 1.5; of cotton, 1.24; of flax-fibre, 1.45. (Kopp. *Ann. Pharm.* 35, 39.)—Inodorous and tasteless.

## Calculation

According to PAYEN and MITSCHERLICH. According to MULDER and BAUMHAUER.

24 C .....	144 .....	44.44 .....	24 C .....	144 .....	43.24
20 H .....	20 .....	6.17 .....	21 H .....	21 .....	6.31
20 O .....	160 .....	49.39 .....	21 O .....	168 .....	50.45
$C^{24}H^{20}O^{20}$ .....	324 .....	100.00 .....	$C^{24}H^{21}O^{21}$ .....	333 .....	100.00

## 1. URE.

## 2. PAYEN.

	Flax.	Cotton.	Amygdal. sativa. a.	Ovule of Apple- blossoms. b.	Sun- flowers. c.	Tissus of Cucumber. d.	Elder- pith. e.
C	42.81	42.11	43.57	44.7	44.1	43.80	43.37
H	5.50	5.06	6.11	6.0	6.2	6.11	6.04
O	51.69	52.83	50.32	49.3	49.7	50.09	50.59
	100.00	100.00	100.00	100.0	100.0	100.00	100.00

## PAYEN.

	Pith of <i>Aeschino- mene.</i> f.	Cotton. g.	Spongioses of the Rootlets. h.	Leaves of <i>Cychorium intyb.</i> i.	<i>Ayланthus glandulosa.</i> at 180°. k.	<i>l.</i>	<i>m.</i>
C	43.39	45.00	44.35	43.00	45.08	43.40	45.95
H	6.33	6.22	6.14	6.18	6.74	6.12	6.19
O	50.28	48.78	49.51	50.82	48.18	50.48	47.86
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

	Woody-fibre from Oak-wood. n.	Spiral vessels of <i>Musa sapient.</i> o.	Inner tissue of the leaves of <i>Agave amer.</i> p.	Seed-wool of <i>Popul. virgin.</i> q.	Woody fibre from Fir-wood. r.	s.	t.	u.
C	43.85	44.53	48.43	43.22	44.70	44.11	51.79	44.38
H	5.86	6.03	6.91	6.50	6.39	6.52	6.23	6.96
O	50.29	49.44	44.66	50.28	48.91	49.37	41.93	48.66
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

	Perisperm of <i>Phytelephas.</i> v.	Cellulose from <i>Cetraria island.</i> w.	<i>Conferva rivularis.</i> x.	<i>Agaricus edulis.</i> y.	<i>Boletus ignarius.</i> z.	<i>Chara hispida.</i> aa.	bb.
C	44.14	44.70	42.57	44.57	44.52	43.40	43.88
H	6.30	6.21	6.52	5.75	6.67	6.11	6.29
O	49.56	49.09	50.91	49.68	48.81	50.49	49.83
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

### 3. FROMBERG.

Cellulose from <i>Cetraria</i> <i>islandica</i> . at 160°.				<i>Agaricus</i> <i>albus</i> . at 150°.			
a.		b.		c.		d.	
C .....	46.68	...	45.85	...	45.57	...	43.94
H .....	6.18	...	6.22	...	6.29	...	6.12
O .....	47.14	...	47.93	...	48.14	...	49.94
100.00				...	100.00	...	100.00
Cellulose from Turnips. at 150°.				Cellulose from White Cabbage. at 140°.			
e.		f.		g.		h.	
C .....	46.26	...	44.12	...	46.80	...	43.43
H .....	6.29	...	6.08	...	6.07	...	6.26
O .....	47.45	...	49.80	...	47.13	...	50.31
100.00				...	100.00	...	100.00
Cellulose from Salad. at 160°.				i.			
				j.		k.	
C .....	48.60	...	44.73	...	48.60	...	44.73
H .....	6.44	...	6.09	...	6.44	...	6.09
O .....	41.96	...	49.18	...	41.96	...	49.18
100.00				...	100.00	...	100.00

## 4. v. BAUMHAUER.

Cellulose from the Perisperm of *Phytelphas*.  
at 140°—150°.

	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	<i>e.</i>
C .....	44.37	43.57	43.65	45.73	43.63
H .....	6.22	6.27	6.31	6.32	6.30
O .....	49.41	50.16	50.04	47.95	50.07
	100.00	100.00	100.00	100.00	100.00
Cellulose from the Shell of <i>Cocos nucifera</i> .					
	<i>at 120°.</i>	<i>at 120°.</i>	<i>at 150°.</i>	<i>at 130°.</i>	<i>at 125°.</i>
	<i>f.</i>	<i>g.</i>	<i>h.</i>	<i>i.</i>	<i>k.</i>
C .....	52.99	47.19	46.32	46.27	43.73
H .....	5.88	6.09	6.01	5.81	6.11
O .....	41.13	46.72	47.87	47.92	50.16
	100.00	100.00	100.00	100.00	100.00

Cellulose from *Cocos lapidea*.  
at 140°.

	<i>l.</i>	<i>m.</i>	<i>n.</i>	<i>o.</i>
C .....	52·21	49·82	49·81	44·19
H .....	5·80	6·01	5·93	6·24
O .....	41·99	44·17	44·26	49·57
	100·00	100·00	100·00	100·00
Cellulose from Peach-kernels.		Cellulose from Walnut-shells.		Cellulose from the Skin of <i>Cytisus Laburnum.</i>
at 140°.		at 140°.	at 140°.	at 160°.
	<i>p.</i>	<i>q.</i>	<i>r.</i>	<i>s.</i>
C ....	52·20	52·13	52·22	49·11
H ....	5·83	6·01	5·91	5·97
O ....	41·97	41·86	41·87	44·92
	100·00	100·00	100·00	100·00
				<i>t.</i>
				45·84
				5·84
				48·32
				100·00
				<i>u.</i>
				44·75
				6·11
				49·14

## V. BAUMHAUER.

5. BLONDEAU  
DE CARROLLES.

Cellulose from the Skin of <i>Ulmus campestris</i> .			Cellulose from the Skin of <i>Liriodendron tulipifera</i> .			Flax.	Cotton.
at 140°.	at 160°.	at 160°.	at 140°.	at 160°.	at 160°.	at 140°.	at 140°.
v.	w.	x.	y.	z.	aa.	bb.	cc.
C 49.53	46.74	43.81	47.76	45.00	44.12	45.14	43.95
H 5.98	5.73	6.08	5.89	5.80	6.11	6.40	6.24
O 44.49	47.53	50.16	46.35	49.20	49.77	48.46	49.81
100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

## 6. MULDER.

<i>Agave americana</i> .			Elder-pith. from the Internodes.	Internodes.	<i>Phytolacca decandra</i> Pith.	Thorns of <i>Cirsium triacanthu</i> at 135°.
Spiral- fibres. at 130°.	Cells of Bass-fibres.			at 140°.		
a.	b.		c.	d.	e.	f.
C .... 47.65	.... 46.98	....	49.28	.... 46.38	.... 45.84	.... 48.44
H .... 6.04	.... 6.11	....	6.01	.... 6.01	.... 6.07	.... 6.99
O .... 46.31	.... 46.91	....	44.71	.... 47.61	.... 48.09	.... 44.57
100.00	.... 100.00	....	100.00	.... 100.00	.... 100.00	.... 100.00

## 7. ROCHLEDER &amp; HELDT.

## 8. ROCHLEDER.

Cellulose from					Cellulose from Coffee-berry. at 130°.
<i>Evernia pruna- stri</i> a.	<i>Lichen rangii- formis</i> b.	<i>Usnea barbat.</i> c.	<i>Ramelina calicaris.</i> d.	<i>Parmetia parietia.</i> e.	
C .... 46.01	.... 46.28	.... 46.47	.... 45.76	.... 45.88	.... 47.07
H .... 6.63	.... 6.75	.... 6.67	.... 6.78	.... 6.55	.... 6.53
O .... 47.36	.... 46.97	.... 46.86	.... 47.46	.... 47.57	.... 46.40
100.00	.... 100.00	.... 100.00	.... 100.00	.... 100.00	.... 100.00

## 9. SCHAFFNER.

Elder-pith.			Pith of Burdock-root.			Sunflower- pith.
at 100°.	at 150°.	at 210°.	at 100°.	at 150°.	at 210°.	at 100°.
a.	b.	c.	d.	e.	f.	g.
C 43.81	.... 47.80	.... 51.09	.... 45.45	.... 48.10	.... 51.39	.... 44.75
H 6.40	.... 6.00	.... 5.59	.... 6.13	.... 5.95	.... 5.40	.... 6.62
O 49.79	.... 46.20	.... 43.32	.... 48.42	.... 45.95	.... 43.21	.... 48.63
100.00	.... 100.00	.... 100.00	.... 100.00	.... 100.00	.... 100.00	.... 100.00

## 10. CHODNEW.

## 11. GLADSTONE. 12. RANSOME.

Pulp of Apple. at 115°.			Pulp of Turnips. at 115°.	Cotton.	Cotton.
a.	b.	c.	d.		
C .... 45.89	.... 45.92	.... 45.94	.... 45.97	.... 44.37	.... 44.20
H .... 6.27	.... 6.28	.... 6.25	.... 6.73	.... 7.24	.... 7.04
O .... 47.84	.... 47.80	.... 47.81	.... 47.30	.... 48.39	.... 48.76
100.00	.... 100.00	.... 100.00	.... 100.00	.... 100.00	.... 100.00



	13. SCHMIDT & HECKER.		14. PETTEN- KÖFER.		15. MITSCHERLICH.		16. KNOP & SCHNEIDER-MANN.	
	Cotton.		Cotton.		Swedish Paper. at 140°.		Cellulose from <i>Cetrar. island.</i> at 80°.	
					a. b.			
C .....	43.27	.....	44.5	.....	44.22	.....	45.82	.....
H .....	6.30	.....	6.1	.....	6.23	.....	6.25	.....
O .....	50.43	.....	49.4	.....	49.55	.....	47.93	.....
	100.00	.....	100.00	.....	100.00	.....	100.00	.....

## 17. SCHLOSSBERGER &amp; DÜPPING.

	Cellulose from Cork. at 100°.		<i>Polyporus fomentar.</i> at 100°.		<i>Daed. querc.</i> at 100°.		<i>Polyporus destruct.</i>	
	a. b.		c. d. e.					
C .....	44.91	.....	45.37	.....	45.52	.....	43.08	.....
H .....	6.05	.....	6.82	.....	6.31	.....	6.24	.....
O .....	49.04	.....	47.81	.....	48.17	.....	50.68	.....
	100.00	.....	100.00	.....	100.00	.....	100.00	.....

## 18. F. SCHULZE.

	Swedish Paper.		Cotton.		Flax.		Straw.		Cellulose from Walnut- Horn- Evergreen shells. beam. oak.		
	a. b.		c. d.		e. f. g.						
C .....	44.10	.....	41.16	.....	44.35	.....	44.58	.....	44.11	.....	42.71
H .....	6.38	.....	6.09	.....	5.97	.....	5.99	.....	6.03	.....	6.05
O .....	49.52	.....	52.75	.....	49.68	.....	49.43	.....	49.86	.....	51.24
	100.00	.....	100.00	.....	100.00	.....	100.00	.....	100.00	.....	100.00

## F. SCHULZE.

## 19. ERDMANN.

## 20. BECHAMP.

## 21. WEBER.

	Alder.		Cellulose from Acacia. Pine.		Cellulose.		From Gun-cotton.		From a Wasp's-nest.	
	h. i.		k. l.							
C 43.96	.....	48.70	.....	44.29	.....	44.05	.....	43.3	.....	52.55
H 5.96	.....	6.20	.....	6.09	.....	6.26	.....	6.3	.....	7.97
O 50.08	.....	45.10	.....	49.62	.....	49.69	.....	50.4	.....	39.48
	100.00	.....	100.00	.....	100.00	.....	100.00	.....	100.00	.....

All the analyses are calculated after deducting the ash.

2. Payen (*N. Ann. Sc. nat. Bot.* 11, 21 and 27; 14, 73): *a*—*i*, natural cellulose in the young state; *k*, twice, *l* and *m*, once purified after preparation by method 1; *n* by means of nitric acid; *o* prepared by method 1; *p* obtained by extraction with aqueous ammonia, hydrochloric acid, alcohol and water; *q* by similar treatment after previous evaporation to dryness with aqueous potash; *r* and *s*, by extraction with water, aqueous ammonia, potash, hydrochloric acid, alcohol and ether; *u* by method 1, treated with chlorine gas; *t* in like manner, but not treated with chlorine; *v*, by method 1, *w* by 8, *x* and *y* by 9; *z* and *aa* prepared by 10; *b* *b* purified by mechanical means.

3. Fromberg, (*J. pr. Chem.* 32, 198): *a*, *c*, *e*, *g*, *i*, by once, *b*, *d*, *f*, *h*, *k*, by twice treating the corresponding vegetable matter with aqueous soda, hydrochloric acid, ether, and alcohol in succession.

4. v. Baumhauer (*J. pr. Chem.* 32, 204, and 210): *a* by exhaustion with ether, alcohol, and water; *b* further treated several times with glacial acetic acid, washed with

hot alcohol and water; *c* — *e* were prepared from the substance used for analysis *a*: viz. *c* by prolonged treatment with boiling aqueous ammonia, and washing with boiling water, glacial acetic acid, water and alcohol, — *d* by exhaustion with hot weak soda-ley, and washing with boiling hydrochloric acid, warm water, alcohol and ether, — *e* by repeated treatment with potash-ley, glacial acetic acid, water, alcohol and ether. — *f* was obtained like *a*, and by subsequent treatment yielded *g* — *k*: viz. *g* by steeping in cold dilute soda-ley, *h* by eight days' digestion therewith, *i* by twice steeping in cold concentrated potash-ley, each time for several weeks; *g*, *h*, and *i* were then further exhausted with water, glacial acetic acid, boiling water, alcohol and ether; *k* was prepared from *f* by treatment with chlorine, cold water, boiling water, alcohol and ether. Similarly *l* was obtained in the same manner and treated like *i*, once for the preparation of *m*, twice for that of *n*. *l* treated like *k* yielded *o*. — *p* and *r* were obtained by exhaustion with ether, alcohol, boiling water, and hydrochloric acid, and *p* treated like *i* yielded the substance *q*. — *s*, *v*, *y*, obtained by exhaustion with ether, alcohol, boiling water and hydrochloric acid, yielded *t*, *w*, *z* by treatment with chlorine, cold water, boiling water, alcohol and ether, and *u*, *x*, *a*, *a*, by five days' steeping in strong potash-ley, washing with cold and hot water, treatment with chlorine and washing. *b* *b* was treated with boiling water and hydrochloric acid, *c* *c* then further with strong potash-ley, chlorine, water, alcohol and ether.

5. Blondeau de Carrolles (*Rev. scient.* 14, 476). — 6. Mulder, *a* — *f* prepared according to 2. — 7. Rochleder & Heldt, *a* — *e* according to 8. — 8. Rochleder, according to 7. — 9. Schaffner, according to 6.

10. Chodnew. *a* prepared by washing with water, alcohol and ether; *b* by exhaustion with dilute sulphuric acid; *c* by treatment with aqueous potash, weak hydrochloric acid, water, alcohol and ether. — 11. Gladstone (*Mem. Chem. Soc.* 3, 412). 12. Ransome (*Phil. Mag.* J. 30, 4). — 13. Schmidt & Hecker (*J. pr. Chem.* 40, 257). — 14. Pettenkofer (*Allg. Zeitung*, 12 Dec. 1846). — 15. Mitscherlich, *b* somewhat decomposed. — 16. Knop & Schnedermann (*J. pr. Chem.* 40, 386) prepared by 8. — 17. Schlossberger & Döpping (*Ann. Pharm.* 52, 113), *a* by 11; *b*, *c*, *e* by exhaustion with hot water, weak aqueous potash, hydrochloric acid and alcohol; *d* as it occurs in nature. — 18. F. Schulze. *a* commercial paper washed; *b* — *l* prepared according to 5. — 19. Erdmann. Cellulose separated by alcohol from a solution of cotton in aqueous cuprammonia. — 20. Béchamp (*Compt. rend.* 37, 134; *Inst.* 1853, 261). Cellulose prepared from gun-cotton, by means of a solution of protochloride of iron. — 21. Weber (*Pharm. Viertelj.* 7, 538; *Pharm. Centr.* 1858, 864): from a wasp's nest (corresponding to the formula  $C^9H^3O^5$ ).

The composition of cellulose corresponds to the formula  $C^{12}H^{10}O^{10}$  (Payen);  $C^{24}H^{20}O^{20}$  (Mitscherlich, Gerhardt, Schulze);  $C^{18}H^{12}O^{11}$  (Gay-Lussac & Thénard);  $C^{18}H^{12}O^{16}$  (Proust);  $C^{86}H^{51}O^{23}$  (Rochleder & Heldt);  $C^{24}H^{21}O^{21}$  (Mulder, v. Baumhauer, Knop & Schnedermann). — According to Reade (*Lond. Ed. Mag. J.* 11, 421) the spiral vessels of plants differ in composition from cellular tissue.

*Decompositions.* 1. Cellulose remains unaltered at common temperatures in *dry air*, but in *moist air* it rapidly passes into decay and putrefaction (see *Wood*). — 2. By *dry distillation* it turns brown and then black, without fusion or sensible tumefaction; emits an empyreumatic odour; yields a limpid, ultimately brown distillate, consisting of water, wood-spirit, empyreumatic oil and vinegar, at the same time giving off combustible gases; and leaves a carbonaceous residue which burns easily and completely in contact with the air. — The pith of the elder tree, of sunflower stalks, and of burdock roots turns brown at  $210^\circ$ , and becomes somewhat tough (Schaffner); cellulose after being browned by heat is less hygroscopic than before (Rumford); even cellulose prepared from coffee-beans smells when heated like that separated from wood and not like burnt coffee. (Rochleder.) — Linen fibre carefully heated in a glass tube till it turns yellow, becomes thinner and more shining than cotton, which, when similarly treated, becomes more distorted and woolly (this character may serve for the detection of cotton in linen). (Böttger, *J. pr. Chem.* 30, 257; *Ann. Pharm.* 47, 329.)

3. Cellulose when *set on fire* burns with flame and without leaving

any residue. — Cotton saturated with aqueous chlorate of potash burns away like gunpowder. (Dumas, *Compt. rend.* 23, 984.) Cellulose mixed with potassium or sodium burns with a bright light and leaves charcoal. (Gay-Lussac & Thénard.) — Paper soaked in a solution of 1 pt. pearl-ash in 4 pts. water, or linen or cotton cloth soaked in a solution of 1 pt. pearl-ash in 2 pts. water, and then dried, chars when held in a flame, but does not take fire. (Kirchhoff, *Scher. Nord. Bl.* 1. 122.) — Cloths repeatedly steeped in alum-solution and then moistened with ammonia, or steeped in chloride of calcium solution, and then treated with carbonate of potash, are difficult to set on fire; and cloths steeped in subacetate of lead, and afterwards moistened with sal-ammoniac, ammonia, or alum, will not take fire at all, but when held in a flame, merely glimmer away like tinder. (Morin, *J. Pharm.* 27, 296; *J. pr. Chem.* 24, 281.) — The combustibility of tissues is diminished, or they are made to burn without flame, by steeping them in aqueous solutions of hydrochlorate, sulphate, phosphate or borate of ammonia, or in mixtures of equal parts of hydrochlorate and phosphate of ammonia, or in borax, or in mixtures of equal parts of borax and sal-ammoniac. (Gay-Lussac, *Ann. Chim. Phys.* 18, 211; *Schw.* 34, 245.) — Tissues are rendered incombustible by steeping them in a solution of sulphate of zinc, and then drawing them through aqueous ammonia, so that oxide of zinc is precipitated upon them (Morin), or by steeping in aqueous sulphate of soda (Smith, *N. Phil. Mag.* 34, 116; *Dingl.* 111, 382), or in aqueous sulphate of ammonia, or in aqueous tungstate of soda of  $28^{\circ}$  Tw. mixed with 3 p. c. phosphate of soda. Tungstate of soda is the only salt that can be used for fabrics which have to be washed and ironed, because the saline film which it leaves on the stuff when dry is smooth and glossy, and allows a hot iron to pass smoothly over its surface, a condition not fulfilled by any of the other salts above-mentioned. The addition of phosphate of soda is to prevent the formation of an insoluble bitungstate. (Versmann & Oppenheim, *Communication read before the British Association*, 15 Sept. 1859; *Pharm. J. Trans.* [2], 1, 385; *Chemical News*, 1860, 20.)

4. Cellulose distilled with *peroxide of manganese* and *sulphuric acid* yields formic acid and a peculiar substance, which may for the most part be removed by distillation after the acid has been neutralised. (Gmelin, *Pogg.* 16, 55.)

5. Cellulose is decomposed, with evolution of carbonic acid by *chlorine* in presence of water and under the influence of heat; a similar reaction is produced by *hypochlorites*. Compare Bastick's statement with respect to starch (p. 84). — Cotton, raw flax, or hemp treated for a long time with aqueous chlorine or chloride of lime becomes pulverulent, and, if heated to redness after being washed and dried, gives off a mixture of carbonic oxide and one or more gaseous hydrocarbons  $C^3H^4$ . (Morin, *Ann. Chim. Phys.* 49, 311; *Bull. univers.* 50, 337; *Schw.* 66, 362.) — Cellulose bleached with chlorine still retains a certain quantity of that element, even after careful washing with water and aqueous alkali. (Leykauf, *J. pr. Chem.* 21, 316.) — On the bleaching of paper-pulp with chloride of lime, see Darnis (*Dingl.* 137, 376); De Koniack (*Dingl.* 144, 359). — By steeping in saturated *chlorine-water*, and moistening after a minute with excess of ammonia, the fibre of *Phormium tenax* becomes bright red; Italian hemp, orange-yellow, darker after a

minute; French hemp, after rotting in tanks, darker, but not so strongly coloured as the fibre of *Phormium tenax*. French linen is less deeply coloured than hemp; cotton but very slightly. (Gaudichaud; Payen; Boussingault, *Compt. rend.* 29, 492.)

6. By dry iodine, moist cellulose is decomposed at 150°, with evolution of carbonic acid, in the same manner as by chlorine. — Cellulose is not coloured by an aqueous solution of iodine (Payen, Schleiden); but it is blued if subsequently treated with oil of vitriol (Payen, Schleiden, Schacht), or if previously boiled with potash (Schleiden, Mitscherlich); also if subjected to the action of a solution of chloride of zinc and iodine (F. Schulze, Schacht, Radlkofer): see Decompositions by oil of vitriol, potash and chloride of zinc.

The cellular tissue of the following plants is directly blued by aqueous iodine: *Cetraria islandica* (Meyer); the embryo cells of *Scholia latifolia*, *Sch. speciosa*, *Hymenaea Courbaril*, *Mucuna urens*, and *Tamarindus indica*, because they consist, not of cellulose but of vegetable amyloid (p. 76) (Schleiden). Trécul (*Compt. rend.* 47, 687) rejects this term, and regards the kind of cellular membrane which is directly blued by iodine as in a state of transition between amorphous starch and true cellulose. He observed the direct blueing by iodine in the cellular tissue of several phanerogamous plants, in the epidermis cells and the lower cuticular tissue of *Ornithogalum pyrenaicum*, *O. narbonense*, *O. longibracteatum*, *Scilla autumnalis*, but not constantly; very faintly also in the embryo-cells of *Tamarindus indica* and *Mucuna urens*; of various degrees of intensity, but always distinct, in the albumen-cells of *Iris pseudo-acorus*, *I. sibirica*, &c., *Tulipa sylvestris*, *Ornithogalum pyrenaicum*, *O. longibracteatum*, *O. narbonense*, &c., *Morob iridioidis*, *Agraphis campanulata*, &c., *Hyacinthus orientalis*, *Uropetalum scrobinum*, *Gladiolus psittacus*, *Muscari racemosum*, *Cypella plumbea*, *Scilla amana*, &c., *Bellevalia romana*, *Polygonatum latifolium*, &c., *Asparagus amarus*, *Libertia paniculata*, &c.; on the other hand, the embryo-cells of *Hymenaea Courbaril* were not blued, and those of *Mimuseps Kummel* only after boiling for a short time with water.

7. By immersion in strong nitric acid, or in a mixture of nitric acid and oil of vitriol, or of nitre and oil of vitriol, cellulose is converted, without dissolving or undergoing any alteration of form, into a mixture of several explosive nitrogenous compounds, called gun-cotton or pyroxylin.—More dilute nitric acid corrodes cellulose, producing substances allied to or identical with starch, gum, pectic acid, and malic acid, and dissolves it after prolonged boiling, in an entirely decomposed state, producing apparently oxalic and suberic acids.

On the formation of gun-cotton (see page 168.)

Cotton, linen, or paper immersed for two or three minutes in nitric acid of sp. gr. 1.5 acquires the texture of parchment and is rendered impervious to light and water, because it becomes covered with a film of xyloidin (p. 106).

Paper immersed in cold strong nitric acid swells up to a jelly, which gives a blue colour with iodine on isolated spots, and therefore contains starch; if the paper is sufficiently decomposed, it leaves, after washing with water—which appears to dissolve malic acid—a translucent brownish, compact, horny mass, which, when heated, softens, swells up, and leaves a shining charcoal. (Gmelin).

Flax and paper become gelatinous by four days' immersion in

fuming nitric acid, nitrous gas being at the same time evolved; after washing with water and aqueous ammonia, the flax is yellow, the paper colourless, and both have the composition and structure of woody fibre,—whence it appears that the acid has merely removed foreign matters, without converting the woody fibre into xyloidin. (Mulder, *J. pr. Chem.* 39, 150).

By immersion for a few seconds in nitric acid of ordinary strength, hemp appears pale yellow, flax remains unaltered, New Zealand hemp (*Phormium tenax*) immediately becomes blood-red; the latter coloration is produced, even after bleaching or after the fibre has been treated with aqueous potash. This reaction may therefore serve for the detection of New Zealand hemp-fibre in fabrics. (Vincent, *Compt. rend.* 24, 542).—The fibres of the following plants are coloured pale-red:—*Cocos nucifera* and *C. aurara*; several species of *Cordyline*, *Pandanus* and *Agave*; *Maurilia flexuosa*; several species of *Cissus*; *Phillandrium aquaticum*, *Raphanus sativus*; *Abaca* from Manilla; two species of *Protrac.* (Gaudichaud; Payen; Boussingault, *Compt. rend.* 24, 542).—The colouring is due to the incrusting substances. (Vincent.) Cotton is scarcely or not at all coloured by nitric acid, whereas animal fibres are coloured permanently yellow. This reaction may serve for the detection of cotton in woollen textures. (Böttger, *J. pr. Chem.* 30, 257; *Ann. Pharm.* 47, 329.)

Swedish paper is not at all decomposed by immersion in cold nitric acid of sp. gr. 1.2, and but slightly in the acid heated to 100° (Mitscherlich).—Deal-shavings boiled with 10 pts. commercial nitric acid and 2 pts. water as long as red vapours are evolved, are converted, with simultaneous formation of oxalic acid, into a white pasty mass which, according to Sacc (*N. Ann. Chim. Phys.* 25, 218) is pectic acid, according to Porter (*Ann. Pharm.* 71, 115), a peculiar acid different from pectic acid. (see *Pectic acid*).

8. By oil of vitriol woody fibre (cotton) is first rendered porous, then dissolved, and the solution yields with water a gelatinous precipitate insoluble in water and destitute of optical rotatory power. By prolonged immersion in the solution, this substance is converted into a second gelatinous mass, also non-rotatory, but soluble in water (soluble woody fibre); subsequently wood-dextrin is formed, a substance having much less rotatory power than dextrin from starch, and converted into sugar by boiling with dilute sulphuric acid. (Béchamp, *Compt. rend.* 42, 1213; *N. Ann. Chim. Phys.* 48, 461; *Ann. Pharm.* 100, 367; *J. pr. Chem.* 69, 449).—Woody fibre heated with moderately concentrated sulphuric acid is first converted into gum, and at the same time into sulpholignic acid (Braconnot); first into dextrin (Payen, *N. Ann. Sc. nat. Bot.* 10, 85), first into starch (Schleiden, Mitscherlich), then into gum (Schleiden), into dextrin (Mitscherlich), and finally—by digestion of the solution diluted with water—into sugar. (Braconnot.) The first product is a peculiar substance, Wackenroder's artificial starch (*N. Br. Arch.* 47, 170), then amyloid, and then dextrin. (Schacht, *N. Br. Arch.* 47, 157).—Amorphous cotton-fibre separated by solution of common salt from its solution in aqueous cuprammonia, is converted into sugar by boiling sulphuric acid, half an hour sooner than cotton in its original organised state. (Schlossberger, *Ann. Pharm.* 110, 247).—Cellulose, prepared from coffee-beans, is converted by 36 hours' boiling with moderately strong sulphuric acid, only

into a mass which dissolves partially, with dark colour, in water. (Rochleder.) When linen or paper is heated with water containing sulphuric acid, in a Papin's digester, to a temperature short of  $200^{\circ}$ , only a small portion of it becomes soluble, and is converted into sugar. (Gmelin.)—On the preparation of sugar and alcohol from sawdust, with sulphuric acid, see Arnould (*Compt. rend.* 39, 807; *Inst.* 1854, 366).

In consequence of these alterations, cellulose which has been treated with sulphuric acid, assumes with iodine, a violet, a blue, and ultimately a wine-red colour. Very young cellular tissue is not coloured blue by iodine after treatment with oil of vitriol, because it does not yet consist of true cellulose or woody fibre; older cellular tissue is blued immediately under the same circumstances, and whereas young cellular tissue treated with iodine and strong sulphuric acid, often turns brown immediately, without blueing, older tissue requires to be treated with concentrated sulphuric acid before it will give a blue colour with iodine; very old tissue requires even to be treated with aqueous potash, before it will give the reaction with iodine and sulphuric acid. (Trécul, *Compt. rend.* 47, 688.)—Cellular tissue is turned blue by iodine, if it has been previously subjected for half a minute to the action of a mixture of 1 pt. water and 3 pts. oil of vitriol (Schleiden; Liebig; Schacht, *N. Br. Arch.* 14, 25); if it be saturated with a moderately strong solution of aqueous biniodide of potassium, and bihydrated sulphuric acid then dropped upon it. (Schleiden). Cotton is coloured green by tincture of iodine, if it has been previously macerated with a mixture of 1 pt. oil of vitriol and 2 pts. water; dark blue, if previously treated with a mixture of 2 pts. oil of vitriol and 1 pt. water. (Reinsch). Amorphous cellulose separated from aqueous cuprammonia, by means of common salt, acquires a fine violet or wine-red colour without previous treatment with sulphuric acid, and if moistened with a drop of oil of vitriol, and then treated with iodine, it exhibits a splendid blue colour (Schlossberger, *Ann. Pharm.* 110, 247).

The acid solution separated by filtration from cellulose altered by sulphuric acid, turns iodine blue, and contains a body which is thrown down by water in white flocks, and by alcoholic iodine as a dark blue precipitate (soluble cellulose? Schw.). (Liebig, Reinsch.)—After cotton has been treated for an hour with oil of vitriol, the acid is no longer precipitated by water. (Mulder, *J. pr. Chem.* 39, 152.)

Cellulose treated with oil of vitriol is not coloured blue by alcoholic iodine, if it has been previously immersed in water (the iodine in this case being merely separated.) (Liebig.) The blued cellulose loses its colour when heated with water, and does not recover it on cooling or after gradual addition of iodine (Liebig); it loses its colour in a large quantity of water (Mulder), especially if triturated with a considerable quantity of water, and then appears rotten; treated with water and alcoholic iodine, it turns brown, from precipitation of iodine; after being treated with oil of vitriol mixed with  $1\frac{1}{2}$  pt. water, it is not blued again by alcoholic iodine, but is decolorised by a large quantity of water, provided however the action of the oil of vitriol has not gone beyond a certain limit (Reinsch),—that is to say, provided unaltered cellulose is still present. (Gm.)

The blueing of cellulose which has been treated with sulphuric acid, by iodine, is due to the formation of starch (Schleiden, Schacht, Reinsch, Mitscherlich); it is no proof of the formation of starch, but results from the formation of a body soluble in the acid but precipitated

by water, and on which the iodine is mechanically deposited as on starch. (Liebig, *Ann. Pharm.* 42, 308.)

On the behaviour of cellulose (cotton) when treated with oil of vitriol and iodine under the microscope, see Schacht (*N. Br. Arch.* 47, 157); Payen (*Compt. rend.* 23, 999); Mitscherlich.

Cellulose, before dissolving in oil of vitriol, swells up and becomes translucent. — This property may be applied to the detection of linen and cotton threads in woollen stuffs: when such stuffs are immersed for a quarter of an hour in oil of vitriol, the linen and cotton fibres swell up to a pasty mass, while the woollen threads remain unaltered. (Böttger, *J. pr. Chem.* 73, 498.) — Further, as cotton dissolves in oil of vitriol more quickly than linen, the admixture of cotton with linen may be recognised as follows. The cloth, after repeated washing with rain-water, boiling with water, and drying, is immersed for  $\frac{1}{2}$  to 2 minutes in oil of vitriol, then cautiously squeezed under water with the fingers, washed with water, dipped for a few seconds in solution of carbonate of ammonia, potash or soda, and dried, after washing with water, and drying between bibulous paper. By this treatment the cotton fibres are dissolved, while the linen fibres are merely rendered thinner and more translucent, according to the duration of the experiment; the cotton-fibres also become transparent after a short immersion, while the linen fibres are still white and opaque. (Kindt, *Ann. Pharm.* 61, 253.)

When paper is immersed for half a minute in oil of vitriol of 66° and immediately washed, first with pure, then with slightly ammoniacal water, a substance very much like parchment is obtained: the *Papyrine* of Poumarède & Figuier (*Mém. sur le Ligneux et sur quelques produits qui lui sont isomères*, Paris, 1847), — the *Vegetable parchment* of Hofmann and Warren De La Rue (*Ann. Pharm.* 112, 243; *J. pr. Chem.* 78, 488). — This substance is prepared, according to Gaine (*Ann. Pharm.* 112, 224) by dipping unsized paper in a mixture of  $\frac{1}{2}$  vol. water and 1 vol. oil of vitriol; according to Hofmann, in a mixture of  $\frac{1}{4}$  to  $\frac{1}{2}$  vol. water and 1 vol. oil of vitriol, and washing with ammoniacal water. If the sulphuric acid is only slightly weaker the transformation is very imperfect; and if the paper be left too long in strong sulphuric acid, or at a temperature above 15°, carbonisation or solution takes place. (Hofmann; compare Reinsch *Dingl.* 156, 156; *Chem. Centr.* 1860, 491; Dullo, *Dingl.* 158, 392; *Chem. Centr.* 1860, 25.)

Such parchments may be formed not only from papers containing flax-fibres, but likewise from those which contain cotton-fibres — from the latter, indeed, more quickly. (Dullo.) They are horny on the surface only; have the composition of pure cellulose; five times the cohesion of the paper from which they are produced, and three-fourths as much as animal parchment; offer considerable resistance to chemical reagents; and when immersed in water, even at the boiling heat, merely soften and swell up, but recover their original state when dry. (Hofmann.)

Swedish paper, immersed for 4 weeks in oil of vitriol, became black and hygroscopic, and contained, after deducting ash, 68.04 p. c. C., 3.37 H., and 27.99 O.; sulpholignic acid was found in the solution; after 12 weeks, it was converted into carbonaceous matter of similar composition. (Marchand, *J. pr. Chem.* 35, 199.)

Cellulose distilled with oil of vitriol (also with phosphoric acid or

*chloride of tin*) yields before carbonisation, a volatile oil, then formic acid (sulphurous acid? Gm.) The volatile oil smells of cinnamon and prussic acid. (Emmet, *Sill. Am. J.* 32, 140; *J. pr. Chem.* 12, 120.) By the use of sawdust or chaff, Stenhouse obtained furfural. (*Phil. Mag. J.* 18, 122; *Ann Pharm.* 35, 301.)

9. Cellulose is converted by strong *hydrochloric acid*, in the same manner as by oil of vitriol, into soluble cellulose and wood-dextrin. (Béchamp.) The solution of cotton in fuming hydrochloric acid, which is precipitable by water, does not possess any optical rotatory power. (Béchamp, *Compt. rend.* 51, 255.)

10. Heated with *benzoic acid* to 200° for 50 or 60 hours, or in contact with benzoic acid and oil of vitriol at ordinary temperatures, cotton forms a compound similar to, or identical with benzo-glucose. (Berthelot, *N. Ann. Chim. Phys.* 60, 111.)—Cotton heated with *butyric acid* and oil of vitriol to 100° for 50 or 60 hours, yields traces of butyro-glucose (Berthelot); and when heated with *stearic acid* to 200° for 50 or 60 hours, it yields stearo-glucose. (Berthelot.)

11. Gaseous *fluoride of boron* blackens cellulose almost instantly. (Berthelot, *Compt. rend.* 47, 227.)

12. Cellulose heated to 150° for several days with concentrated aqueous *ammonia*, is converted into a solid, brown, gummy mass, which has a bitter taste, smells when heated like roast meat, and deliquesces on exposure to the air. Its solution may be decolorised by animal charcoal, and is precipitated by infusion of galls. This mass fused with sticks of potash gives off a quantity of ammonia corresponding to 2.5—3 p. c. nitrogen, but it does not give off ammonia when boiled with potash-ley or milk of lime. (Schützenberger, *Zeitschr. Ch. Pharm.* 4, 65. — Comp. P. Thenard, *Compt. rend.* 52, 444; abstr. *Rép. Chim. pure*, 3, 207.)

13. When cellulose is heated with 3 pts. of *melting potash* and a small quantity of water for a long time, and at last nearly to redness, it gives off hydrogen with intumescence and without separation of charcoal, and forms oxalate of potash. (Gay-Lussac, *Ann. Chim. Phys.* 41, 398; *Pogg.* 17, 171; *Schw.* 58, 87.)—Caustic potash at high temperatures forms from cellulose, first formic acid, then ulmic acid. (Péligot, *Compt. rend.* 9, 135.)—*Aqueous potash* of sp. gr. 1.5 boiled with cellulose dissolves it with brown colour; the ulmic acid contained in the solution disappears on heating the liquid to 200° — 225° for four or five hours, oxalic, acetic, formic, and carbonic acids being formed at the same time. 100 pts. of sawdust and 300 pts. hydrate of potash yield 70 pts. of oxalic acid, which decomposes partially when the solution is strongly heated. (Possoz, *Compt. rend.* 47, 907; *J. pr. Chem.* 76, 314.) When paper is fused with 4 pts. hydrate of potash, the pale yellow mass which forms with strong intumescence, contains oxalic acid, yielding a quantity of oxalate of lead equal to 46.4 p. c. of the weight of the paper. (Buchner & Herberger, *Repert.* 38, 189.)

Cellulose moistened with water, and heated in a retort with an equal weight of hydrate of potash, yields hydrogen and a large quantity of wood-spirit. (Péligot, *Ann. Chim. Phys.* 72, 208.)—Wood-shavings and linen heated in like manner with aqueous potash till the liquid is evaporated down, give off a small quantity of water and



empyreumatic oil; while the residue contains acetate of potash and a humoïdal substance precipitable by acids. (Braconnot.) The same mixture more strongly heated gives off carburetted hydrogen gas, and the residue in contact with water and oxygen forms humoïd substance. (Chevreul, *Mém. du Mus.* 1825, 379; Sprengel, *Kastn. Arch.* 81, 170.)

Cellulose is not altered by boiling with weak potash-ley (Payen); by strong potash-ley it is converted into starch (Schleiden); dissolved with previous intumescence and converted into sugar. (Barreswil & Rilliet, *N. J. Pharm.* 21, 205.) Hence cellulose boiled with aqueous potash or with hydrate of potash acquires a colour varying from violet to blue (Mitscherlich); similarly, vegetable cellular tissue mixed with aqueous potash and evaporated down to a saline crust, loses its colour again when boiled with water; becomes blue with iodine only when again treated with potash, and is finally converted by treatment with potash into ulmin. (Schleiden, *Ann. Pharm.* 42, 301.)—The property of linen-fibre to acquire a deep yellow colour by boiling with a mixture of equal quantities of water and potash-hydrate, whereas cotton is little or not at all coloured by it, is applied by Böttger (*J. pr. Chem.* 30, 257; *Ann. Pharm.* 47, 329) to the detection of cotton in linen.

14. A concentrated aqueous solution of *chloride of zinc*, heated with cellulose, dissolves it with tumefaction, but without colour; and converts into a modification of cellulose, afterwards into sugar. (Barreswil & Rilliet, *N. J. Pharm.* 21, 205; *J. pr. Chem.* 56, 58.)

As soon as cellulose comes in contact with aqueous chloride of zinc, it is coloured dark blue by iodine (Barreswil & Rilliet); hence it is immediately blued by an aqueous solution of *iodated chloride of zinc* (F. Schulze), although no gradual solution or change of form takes place. (Radlkofer, *Ann. Pharm.* 94, 332.)—To prepare the solution of iodated chloride of zinc, a solution of zinc in hydrochloric acid is evaporated to a syrup with excess of zinc; iodide of potassium is dissolved in it to saturation; iodine is then added, and the liquid is diluted, if necessary, with water (Schacht, *Das Mikroskop*, &c., Berlin, 1851, 31); or better, the neutral syrup is diluted with distilled water to sp. gr. 1·8 at 15°, and 6 p. c. iodide of potassium is dissolved in it, together with as much iodine as it will take up. (Radlkofer.)

Paper dipped into a strong solution of chloride of zinc, is converted, in the same manner as by sulphuric acid, into vegetable parchment. (Dallo, *Dingl.* 158, 392; *Chem. Centr.* 1861, 25.)

15. When an aqueous solution of *bichloride of tin* is left to dry upon cotton or linen, and then heated to 120° — 130°, the substance is blackened in consequence of the formation of caramelin. (Maumené, *Compt. rend.* 30, 314; 39, 422.)

16. Cellulose is not *fermentable*. When slices of fresh potatoes are immersed in water at low temperatures, together with slices of putrifying potatoes, the cells of the fresh potatoes separate from one another, and the filtered water contains a ferment which decomposes slices of fresh potatoes in the same manner; the disintegrated cellular tissue finally dissolves, whereas the starch-granules remain unaltered. The ferment thus produced acts only upon cellulose; just as in the potato-disease, only the cellulose is attacked.

*Combinations.* Cellulose is insoluble in water.

With *Bases*.—Woody fibre (linen) absorbs from 70 — 100 volumes of ammonia gas. (Walter Crum, *Ann. Pharm.* 55, 221.)

*Cellulose with Potash.* When calico is immersed for 10 to 30 minutes in syrupy potash-ley, and then washed with alcohol of sp. gr. 0·825, it shrinks on drying to  $\frac{1}{16}$ , and contains 14·72 p. c. potash, corresponding to the formula  $C^{24}H^{20}O^{20}, KO$  (calc. 14·59 p. c.) Gladstone. (*Chem. Soc. Qu. J.*, 5, 17.)

*Cellulose with Soda.*—When calico is immersed for 10 — 30 minutes in soda-ley of sp. gr. 1·342, and then washed with hot alcohol of sp. gr. 0·825 it shrinks by one-fourth on drying, and contains, on the average 9·68 p. c. soda, corresponding to the formula  $C^{24}H^{20}O^{20}, NaO$  (calc. 9·65 p. c.). Common unwoven cotton forms a similar compound; prolonged immersion or the use of stronger soda-solution appears to produce partial solution and decomposition. Cotton likewise unites with soda in other proportions, but never with a greater quantity than that contained in the compound above-mentioned. Water extracts all the soda from the compound, leaving a more contracted fibre, which, when dried, has a more brilliant aspect than ordinary woody fibre. (Gladstone, *Chem. Soc. Qu. J.* 5, 17; *J. pr. Chem.* 56, 247.) ¶ Cotton passed through a solution of caustic alkali of 35°—39° Bm., then washed in water, in dilute sulphuric acid, and again in water, contracts both in length and breadth, acquires increased tenacity, and takes colours much better than ordinary cotton. The amount of alteration varies according to the strength of the solution. The same effect is produced by sulphuric acid of 48° Bm. at 37·5°, and by chloride of zinc solution of 64° Bm. at 65°—71 $\frac{1}{4}$ °. (Mercer, *Rep. Patent. Invent.* 1851, 358; *Dingl.* 121, 438; *Lieb. Kopp. Jahresber.* 1851, 747.) ¶

Cotton does not separate alumina from solution of *alum* or *acetate of alumina*, (Walter Crum, *Phil. Mag.* 35, 334; *J. pr. Chem.* 50, 123; Erdmann & Mittenzwey); but if the solution of acetate of alumina, ferric acetate, or other salt containing a volatile acid is left to dry upon cotton, the salt is decomposed after a short time, the acid volatilises, and the base is precipitated on the cotton in so close a state of union, that it cannot be removed by washing with water. This combination is merely mechanical, and is limited to the inner surface of the cotton-fibres forming a tube. (Walter Crum, *Ann. Pharm.* 55, 223).—The structure of cotton has no influence on its relation to the solutions of metallic salts; organised cotton digested for 24 hours with cold-saturated aqueous solution of alum at 40° — 50°, took up no sulphuric acid, and only traces of alumina; amorphous cellulose separated from an aqueous solution of cuprammonia did not take up any thing from a 10 per cent. solution of alum. (Erdmann & Mittenzwey.)

The dyeing of cotton depends upon its mechanical surface-attraction for certain colouring matters. (Walter Crum, Erdmann & Mittenzwey), consequently organised as well as amorphous cotton may be dyed (Bolley, *Ann. Pharm.* 106, 235; *Dingl.* 148, 142; *J. pr. Chem.* 74, 381); but it does not take up solutions of metallic salts or mordants (Verdeil, *Compt. rend.* 47, 961; *J. pr. Chem.* 77, 58).—To dye cotton, flax, and hemp, in such a manner that they may not lose their colour by washing or rubbing, the colouring matter which has penetrated the fibre must be rendered insoluble, since these fibres, unlike those of

wool or silk, do not possess any actual attraction for colouring matter mixed with mordants. (Verdeil.)—Runge regarded dyed cotton as a chemical compound of the mordant-base, colouring matter, and woody fibre; but since dyed cotton dissolves for the most part in an ammoniacal copper-solution, just like woody-fibre, leaving the mordant-base and the colouring matter undissolved, this view can scarcely be correct. (Bolley, *Ann. Pharm.* 106, 235; *J. pr. Chem.* 94, 381).

Cotton digested even for a long time with *hydrated ferric oxide* does not take up any of the oxide. (Verdeil.)

*With Copper.*—Cellulose dissolves in aqueous *basic hyposulphate* or *basic sulphate of cuprammonium* (Schweizer, *J. pr. Chem.* 72, 109; *Chem. Centr.* 1858, 49); most easily in aqueous *basic carbonate of cuprammonium* (Schweizer, *J. pr. Chem.* 76, 344), in aqueous *oxide of cuprammonium* (Peligot, *Compt. rend.* 47, 1034).—Erdmann (*J. pr. Chem.* 76, 385) maintains—in opposition to the opinion of Schweizer, Cramer, and others—that this liquid is not a true homogeneous solution, but a liquid similar to gelatinous starch, merely containing the cellulose in a swollen state.

To prepare the copper-solution (called *Cuoxam* by Cramer), basic hyposulphate of copper ( $4CuO, S^2O^6$ ) or basic sulphate of copper, is dissolved in aqueous ammonia; or the precipitate formed by carbonate of soda in a solution of sulphate of copper, is dissolved, after washing and moderate drying, in aqueous ammonia of sp. gr. 0.945 (Schweizer); or recently precipitated hydrated cupric oxide is dissolved in strong aqueous ammonia (Schlossberger); or aqueous ammonia, mixed with a few drops of sal-ammoniac (Schweizer), is made to trickle through copper turnings (Peligot); through *cementation-copper*, that is to say, metallic copper obtained by precipitation. (Peligot.)—The solvent power of the copper-solution for cellulose increases with the amount of copper contained in it, and is diminished or completely annihilated by acids, salts, or sugar. (Schlossberger.)

Cotton immersed in aqueous biphosphate of cuprammonium becomes first gelatinous, then slippery, and forms an almost transparent gummy liquid, which may be filtered after addition of water. The cotton-fibre before dissolving in the ammoniacal copper-solution, becomes darker in colour than the liquid itself. The degree in which it swells up depends upon the concentration and mass of the acting solution; in excess of the concentrated copper-solution, it dissolves instantly without previous tumefaction (Cramer.) The act of solution is not attended with evolution of heat. (Schweizer.)

Paper (Schweizer), hemp, and flax-fibre are acted upon by the ammoniacal copper-solution in the same manner as cotton, excepting that flax-fibre is not uniformly attacked, and consequently swells up in knots here and there, and shortens at the same time, before dissolving. Many uni-cellular algæ, many fungi, a few lichens, the bass-fibres of *Cinchona rubra*, the pith-cells of *Hoya carnosa*, pappus-hairs, the clavate masses of cellulose in the epidermal cells of *Ficus elastica*, and cork (also the spongy cellular tissue of mushrooms: *Fremy*) are not at all altered by the ammoniacal copper-solution; the wood-cells of *Taxus baccata* and *Quercus* are but slightly coloured by it; the wood-cells of *Pinus*, and the cells of *Fucus vesiculosus*, *Caulerpa prolifera*, &c., more distinctly; in most cases, however, wood-cells swell up in the

solution, and then dissolve more or less quickly. (Cramer.)—From some plant-cells aqueous cuprammonia dissolves the pure cellulose of the outer membrane, leaving an inner membrane, which turns green, and when treated with acids yields pectic acid; other cells are not at all altered by the copper-solution. Thus the bass-fibres of all plants and the utricular tissue of fruits dissolve immediately, whereas the pith of trees and the fibrous tissue of wood remain undissolved. (Frémy, *Compt. rend.* 48, 202 and 275.)—In cases in which the action of the aqueous cuprammonia on woody fibre takes place slowly or not at all, it is generally the presence of foreign matters in the wood-cells that prevents the solution from coming in contact with the woody fibre; hence, in many cases, the action of the copper-solution may be brought about by finer comminution of the woody fibre, or by boiling it with nitric acid and chlorate of potash. (Cramer.) The insolubility of woody fibre in aqueous cuprammonia may also be caused—independently of the presence of foreign bodies mixed or combined—by its state of aggregation, or because the contact of the solution with the cellular tissue is prevented by the presence of air between the fibres. The pith of plants, which is insoluble in aqueous cuprammonia, dissolves when cut up. By trituration in cold water, 45 p. c. is rendered soluble, or 75 p. c. if the insoluble pith has been dried in vacuo at 110° before trituration. Hackled flax, and even that which has been steeped in warm water, withstands the action of the copper-solution for more than six hours, whereas the fibre of Swedish paper dissolves in it immediately; hence no conclusions as to the existence of isomeric modifications of cellulose can be drawn from its more or less easy solubility in aqueous cuprammonia. (Payen, *Compt. rend.* 48, 772.) Those kinds of cellulose which are insoluble in aqueous cuprammonia (excepting the spongy tissue of mushrooms) are rendered soluble by boiling with dilute acids or aqueous alkalis. (Frémy, *Compt. rend.* 48, 275.)—The solubility of cotton in aqueous cuprammonia is not diminished by dyeing or mordanting; it still dissolves, leaving the colouring matter and the mordant. (Bolley, *J. pr. Chem.* 74, 381; *Ann. Pharm.* 106, 235.)

Aqueous cuprammonia dissolves a quantity of cellulose equal in weight to the copper which it contains. (Peligot.) Its solvent power is limited; for when poured upon excess of cotton, it loses in a few minutes its capacity of dissolving fresh quantities of cotton, not even causing them to swell up. (Cramer.)

The solution of cellulose in cuprammonia is precipitated by a large quantity of water, even without loss of ammonia by evaporation, and the more abundantly the longer it stands (Cramer, Schlossberger, Payen, Erdmann); by acids in excess (Schweizer, Cramer, Payen), or even by a quantity of acid not sufficient to saturate the ammonia (Payen); by salts, even by sulphate of copper; also by sugar, honey, a thick solution of dextrin or gum, and by alcohol, but not by a strong aqueous solution of urea, by chloroform or by ether. The solution when boiled gradually acquires a light blue turbidity, and on addition of potash deposits black oxide of copper. (Schlossberger.)

The flocculent precipitate obtained with water, acids, salts, sugar, &c., is amorphous cellulose; it possesses all the properties of ordinary cellulose excepting the structure (even the colouring power, according to Bolley), and when dried, appears more or less grey, translucent,

brittle, tasteless, not glutinous, and resembles dried starch-paste (Schweizer); if separated by alcohol, it is white after careful washing and drying. (Erdmann.)

In contact with *basic acetate of lead*, cellulose (filtering paper) swells up considerably, rendering filtration impossible, and after 48 hours is converted into a loose thread-like tissue. The compound formed after sufficiently prolonged contact contains, after washing with hot water, 33.1 p. c. oxide of lead ( $3 PbO, 2 C^{24}H^{20}O^{20} = 34.1$  p. c.) (Vogel, *N. Repert.* 6, 239.)

Cotton immersed in a solution of *plumbate of lime* (obtained by mixing neutral acetate of lead with lime till the resulting precipitate is redissolved), abstracts the lead. (Walter Crum, *Ann. Pharm.* 55, 227.)

In aqueous solution of *nickel-ammonia*, cellulose does not swell up, but remains colourless and undissolved. (Schlossberger, *J. pr. Chem.* 73, 369.)

In the *indigo-vat*, cellulose turns yellow, and on exposure to the air, blue; but no chemical compound of cellulose with indigo is formed (Walter Crum); it is not coloured by solution of indigo or of carmine and has no attraction for these colouring matters. (Maschke, *J. pr. Chem.* 76, 47.)

Cellulose is insoluble in *alcohol*, in *ether*, and in *oils* both *fixed* and *volatile*.

### *First Appendix to Cellulose.*

1. *Paracellulose*.—The utricular tissue of the wood which forms the medullary rays; hence also in the pith of trees.—Soluble in *oil of vitriol*, strong *hydrochloric acid*, and strong boiling *potash-ley*. Insoluble in aqueous *cuprammonia*, but becomes soluble after 24 hours' boiling with water, or by treatment with acids or aqueous alkalis. (Freymy, *Compt. rend.* 48, 667 and 862; *N. J. Pharm.* 35, 321 and 401; abstr. *Inst.* 1859, 121 and 151.)

2. *Vasculose*.—The constituent which forms the vessels of wood. To obtain it, the vessels, as they occur in nature, are first treated with *potash-ley* to remove albuminoids, pectinoids and tannin, then repeatedly with *hydrochloric acid*, increasing the strength each time, and with cold *oil of vitriol* to remove utricular and fibrous tissues; and the residual matter is washed with water, alcohol, and ether.—Vasculose is insoluble in concentrated acids, soluble in strong boiling *potash-ley*; insoluble in aqueous *cuprammonia*, (Freymy, *Compt. rend.* 48, 862; *N. J. Pharm.* 35, 401; abstr. *Inst.* 1859, 151; *Rép. Chim. pure*, 1, 433.)

3. *Fibrose*.—The substance which forms the fibres of wood.—Wood-shavings are boiled with strong *potash-ley*, and washed with water, alcohol, and ether.—White, easily turns mouldy; according to Decaisne, it exhibits under the microscope, the structure of woody fibre, only somewhat enlarged by the prolonged action of the alkali.—It dissolves in *oil of vitriol*, without passing into *dextrin*, and is separated from the solution by water as a thick translucent jelly. It is insoluble in *potash-ley* and in aqueous *cuprammonia*. (Freymy, *Compt. rend.* 48, 862;

*N. J. Pharm.* 35, 401; abstr. *Inst.* 1859, 151; *Rép. Chim. pure*, 1, 433.)

4. *Cutin*.—In the epidermis (*cuticula*) of leaves, petals and fruits, together with woody fibre, albumin, pectinoid substances and fat. (Freymy.)—According to Payen (*Compt. rend.* 48, 775) all the external parts of plants, viz., the epidermis and cuticle, consist of cellulose impregnated with fats, nitrogenous bodies, and inorganic salts; he denies (*Compt. rend.* 48, 893), the presence of any peculiar substance not containing nitrogen or woody fibre.

The cuticle of leaves, or the leaves themselves, are boiled for half an hour with weak hydrochloric acid and washed with water; the woody fibre is removed from the residue by aqueous cuprammonia; and the undissolved portion is treated successively with water, hydrochloric acid, weak aqueous potash, alcohol, and ether. (Freymy.)

Cutin exhibits under the microscope, the aspect of an amorphous perforated film. It is very extensible, contains 78.66 p. c. C., 11.37 H., and 14.97 O., approaching in composition to the fats. (Freymy.)—According to Payen (*Compt. rend.* 48, 893), it is a product of the transformation of the cuticle by the reagents above-mentioned, and not a peculiar constituent contained therein.

It decomposes when *heated*, producing fatty acids. It is not decomposed by cold *nitric acid*, but when boiled with that acid yields all the products that are formed in like manner from the fats, especially suberic acid. It is not altered by contact with cold *oil of vitriol* or boiling *hydrochloric acid*. It is saponified by boiling concentrated aqueous potash, and from the soap thus formed, a liquid fatty acid may be separated, which is soluble in alcohol and ether, but appears to be different from oleic acid. Cutin is not altered by dilute aqueous *alkalis*, by *ammonia*, or by any neutral solvent.

Cutin is insoluble in aqueous *cuprammonia* also in *ether* (Freymy. *Compt. rend.* 48, 669; *N. J. Pharm.* 35, 321; abstr. *Inst.* 1859, 121; *Rép. Chim. pure*, 1, 357).

## 5. Suberin.

FOURCROY. *Système*, 8, 98; *Scher. J.* 8, 288.

CHEVREUL. *Ann. Chim.* 62, 323; *N. Gehl.* 5, 379.—*Ann. Chim.* 96, 155; *Schw.* 16, 327.

DÖPPING. *Ann. Pharm.* 45, 290.

MITSCHERLICH. *Ann. Pharm.* 75, 310; *J. pr. Chem.* 50, 148.

### *Korkstoff.*

First investigated by Brugnatelli, then by Bouillon-Lagrange, Fourcroy, Link, and others.—It is the chief constituent of the outer bark of *Quercus Robur*; forms the cuticle of other plants (Fourcroy), sometimes the amorphous coherent integuments of the entire plant, sometimes only the external cellular layer of the stem, very often several layers, as in potatoes; it also forms a film over the most delicate hairs of plants, which, like cotton, are difficult to wet with water, unless the cork has been previously removed by oxidising substances. (Mitscherlich.)—Resembles Freymy's cutin.—It is modified woody fibre. (Gerhardt, *Traité*, 2, 485.)

Rasped cork is exhausted successively with water and alcohol (Chevreul), with ether, alcohol, and water (Mulder, *J. pr. Chem.* 39, 155), and afterwards with dilute hydrochloric acid, which treatment, however, does not remove cork-resin (xiii. 204), a nitrogenous substance, or woody fibre. (Döpping.)

Very light, soft, and elastic; of cellular structure. Reddish grey (Döpping). Not easily wetted by water.

	Mulder. at 130°.		Döpping.		Mitscherlich.	
	<i>a</i>		<i>b</i>		<i>c</i>	<i>d</i>
C .....	65·52	.....	67·3	.....	62·30	65·73
H .....	7·97	.....	8·7	.....	7·15	8·33
N .....			2·3		3·03	1·50
O .....			21·7		27·52	24·44
			100·0	.....	100·00	100·00

*a* and *b* from cork; *c* from potatoes; *d* from cork, carefully purified from the brown substances which envelop it. It is not exactly known whether the nitrogen is an essential constituent of the suberin itself, or exists only in the substances which adhere to it.

Suberin yields by *dry distillation*, gases, a small quantity of acid water, a colourless, or brown oil, a small quantity of ammonia, a crystalline oil which melts when heated, and a sublimate which volatilises with a fatty odour, and leaves an easily combustible charcoal aggregated here and there in lumps. (Chevreul.)—It *burns* easily in the open fire, with tumefaction and brilliant white flame (Chevreul), emitting a peculiar odour like that of crude cork (Döpping), and leaving a soft, loose, tumefied coal. (Chevreul.)—*Chloride of iodine* converts it, with evolution of hydrochloric acid, into a mass which contains chlorine and iodine; gives up those elements to water when boiled with it; and leaves a brown-black, tough, glutinous mass, insoluble in water, soluble in aqueous alkalis, alcohol, and ether, yielding by distillation iodine, hydrochloric acid gas, carbonic oxide, and carburetted hydrogen, and leaving a carbonaceous residue. (Casaseca, *J. Pharm.* 12, 620; *J. pr. Chem.* 17, 151.)—It is oxidised by *nitric acid* of sp. gr. 1·2, even below 100°, the cells becoming soluble with tumefaction in aqueous potash, and separating from one another; at the same time reddish products are formed, which melt in the boiling acid and are soluble in alcohol, and ultimately suberic and succinic acid.—Cork, the suberin of potatoes, and the cuticle of *Aloe lingua* yield similar products in variable quantities, any woody fibre that may also be present remaining insoluble in the acid, even if the mixture be heated over the water-bath till no more red fumes are evolved. The suberin of potatoes yields, with nitric acid, 6 per cent. of a fatty acid soluble in alcohol; common cork yields 39·67 p. c. of a fatty acid, leaving 2·55 p. c. woody fibre. (Mitscherlich.)—Suberin treated with nitric acid forms oxalic acid (Chevreul, Döpping); if first macerated with 6 pts. nitric acid of sp. gr. 1·28, and then distilled, it yields a nitro-resin, suberin, oxalic acid, ammonia, and artificial bitter, leaving woody fibre. Common cork yields with nitric acid, the same products, together with traces of benzoic acid, giving off nitrous gas, carbonic acid, hydrocyanic acid, and acetic acid. (Chevreul)—*Oil of vitriol* blackens cork, does not form gum from it (Vogel), but when heated slowly forms brown products. (Mitscherlich.)

## 6. Wood.

- FOURCROY. *Système des connaissances chimiques*, 8, 87.  
 PROUST. *J. Phys.* 48, 469; *Scher. J.* 7, 707.  
 SAUSSURE. *A. Gehl.* 4, 681.  
 RUMFORD. *Schw.* 8, 160.  
 BRACONNOT. *Ann. Chim. Phys.* 12, 172; *Schw.* 27, 328; *Gillb.* 63, 347.  
 PAYEN. *N. Ann. Sc. nat. Bot.* 11, 27; abstr. *Compt. rend.* 8, 51; *J. pr. Chem.* 16, 436.  
 V. BAUMHAUER. *Scheik. Onderzoek.* 2, 62; *J. pr. Chem.* 32, 204.—*Repert.* 95, 220.  
 BAER. *N. Br. Arch.* 56, 159.  
 CHEVANDIER. *Arch. phys. nat.* 8, 5; *N. Ann. Chim. Phys.* 10, 136.—*Report, Compt. rend.* 24, 269.  
 VIOLETTE. *N. Ann. Chim. Phys.* 23, 475; abstr. *Compt. rend.* 26, 683; *Dingl.* 109, 137.  
 F. SCHULZE. *Beiträg. z. Kenntniss d. Lignins*, Rostock, 1856; abstr. *Chem. Centr.* 1857, 321.  
 FREMY. *Compt. rend.* 48, 862, 275; *Pharm. Viertelj.* 9, 221.

*Decomposition of Wood.*

- REICHENBACH. *Schw.* 59, 436.—61, 175, 273, 464.—62, 46, 129, 273.—65, 295, 461.—66, 301.—67, 1, 57, 274.—68, 1, 57, 223, 239, 295, 351, 399.—69, 19, 175, 241.—*Ann. Pharm.* 2, 253 and 259.—8, 216.—24, 238.  
 GREGORY. *Ann. Pharm.* 21, 143.  
 LIEBIG. *Ann. Pharm.* 30, 264.  
 HERMANN. *J. pr. Chem.* 27, 165.  
 MULDER. *Scheik. Onderzoek.* 2, 76; *J. pr. Chem.* 32, 321.  
 VIOLETTE. *N. Ann. Chim. Phys.* 23, 475; abstr. *Compt. rend.* 26, 683; *Dingl.* 109, 137.—*N. Ann. Chim. Phys.* 32, 304; *J. pr. Chem.* 54, 313; abstr. *Pharm. Centr.* 1851, 530.—*N. Ann. Chim. Phys.* 39, 850; abstr. *Pharm. Centr.* 1853, 376; *J. pr. Chem.* 59, 332.  
 CAGNIARD LATOUR. *Inst.* 1850, 214, 253.  
 GÜPPERT. *Pogg.* 72, 174; *J. pr. Chem.* 42, 56.  
 PETTENKOFER. *N. Repert.* 3, 74, *N. Jahrb. Pharm.* 1, 360; *J. pr. Chem.* 62, 508; *Pharm. Centr.* 1854, 601.  
 VÖLCKEL. *Pogg.* 82, 496; abstr. *Ann. Pharm.* 80, 306; *Pharm. Centr.* 1851, 470.—*Pogg.* 83, 272 and 557; abstr. *Ann. Pharm.* 80, 309; *Pharm. Centr.* 1851, 870; *J. pr. Chem.* 54, 181.—*Ann. Pharm.* 86, 66; abstr. *J. pr. Chem.* 60, 68.  
 CAHOUS. *Compt. rend.* 30, 319; *Pharm. Centr.* 1850, 344.  
 FEHLING. *Ann. Pharm.* 106, 388.  
 FRITZSCHE. *J. pr. Chem.* 82, 321.

*Distillation products of Peat, Lignite, and Coal.*

- RUNGE. *Pogg.* 31, 65 and 512.—32, 308, 323.  
 HOFFMANN. *Ann. Pharm.* 48, 1.  
 LAURENT. *N. Ann. Chim. Phys.* 3, 195.



- MANSFIELD. *Chem. Soc. Qu. J.* 1, 244; *Ann. Pharm.* 69, 168; *Pharm. Centr.* 1849, 376.
- RITTHAUSEN. *J. pr. Chem.* 61, 74.
- WILLIAMS. *Ed. N. Phil. J. N. Ser.* 2, 324; *Pharm. Centr.* 1855, 856; *J. pr. Chem.* 67, 247. — *Phil. Mag.* [4] 13, 134; 14, 223; *Ann. Pharm.* 102, 126; *J. pr. Chem.* 72, 176; *Pharm. Centr.* 1857, 254. — *Phil. Trans.* 1857, 447. — *Phil. Trans.* 1857, 3, 737; *Ann. Pharm.* 108, 384; *J. pr. Chem.* 74, 253; 76, 340. — *Chem. Soc. J.* 15, 130.
- CHURCH. *Phil. Mag.* [4] 13, 415; *Ann. Pharm.* 104, 111; *J. pr. Chem.* 72, 124; *Chem. Centr.* 1857, 927.
- VOHL. *Ann. Pharm.* 98, 181. — 103, 283. — *Dingl.* 143, 363 — *Ann. Pharm.* 107, 45. — 109, 192. — *Dingl.* 152, 306 and 390; abstr. *Chem. Centr.* 1859, 490 and 517.
- FRESENIUS. *Nassauische Gew. Ver. Mitth.* 1855, 13 and 14; *Dingl.* 133, 129; abstr. *Chem. Centr.* 1856, 242.
- WAGENMANN. *Dingl.* 145, 309; abstr. *Chem. Centr.* 1857, 691.
- MÜLLER. *Dingl.* 146, 210; abstr. *Chem. Centr.* 1858, 47.
- SULLIVAN. *Atlantis* 1, 185; *Kopp's Jahresber.* 1858, 280.
- CRACE CALVERT. *Compt. rend.* 49, 262; *Kopp's Jahresber.* 1859, 742.
- HESS. *Dingl.* 153, 380; abstr. *Chem. Centr.* 1860, 164.
- THENIUS. *Ueber einige neue organische Basen des Steinkohlentheers*, Göttingen, 1861.

Wood consists, according to Payen, v. Baumhauser, and Schulze of cellulose or woody fibre, which forms the cell-walls, and of incrusting substances deposited thereon (*Sclerogen*, *Lignin* = products of decomposition of the decaying cells [Schleiden, *Grundz. d. wiss. Botanik*, Leipzig, 1849, 1, 172]). Fremy denies the existence of incrusting substances, and supposes that the true woody tissue consists of *vasculose*, which is insoluble in oil of vitriol, soluble in boiling concentrated potash-ley, *paracellulose* soluble in oil of vitriol and in boiling potash-ley, and *fibrose* soluble in oil of vitriol, but insoluble in boiling concentrated potash-ley (see page 144). Wood likewise contains the following substances in variable quantities, varying with the season and locality, and with the species and age of the plant:—the constituents of the sap, such as albuminoidal substances (0·81—0·12 p. c. nitrogen, according to Chevandier), sugar, gum, tannic acid, &c., colouring matters, starch (only in autumn and winter), pectose, according to Fremy (Payen found none), resins and volatile oils, and the ordinary mineral constituents of plants.

The external properties of the wood depend, partly on the mode of union of the fibres (ivory or fibrous texture), partly on the proportions between the essential or adventitious proximate constituents. Hence the several species of wood differ greatly in hardness, colour, and apparent specific gravity. The latter, that is to say, the specific gravity of the wood air-dried, but still *containing air*, varies, according to Karmarsch (*Grundz. d. mech. Technologie*, 635), from 0·383 (poplar-wood) to 1·342 (logwood). The actual specific gravity of different kinds of wood is tolerably uniform, 1·5, according to Violette; from 1·46 (maple) to 1·53 (oak), according to Rumford. Wood always contains a larger quantity of carbon than cellulose; its composition varies between very wide limits (according to the nature of the incrusting substances: *Payen*), as much apparently in the same as in different woods. The lowest and highest amounts actually found are: 46·10

p. c. C., (beech-wood) Baer, and 54.44 p. c. (oak-wood) Payen; (beech-wood = 54.35);—5.55 p. c. H., (box-wood) Prout, and 6.40 p. c. (aspen-wood) Payen;—39.32 p. c. O., (oak-wood) Payen, and 46.87 p. c. (beech-wood) Baer.

*Decompositions.* 1. Wood may be heated to 150° without sensible alteration. At a higher temperature, decomposition begins, its course being different according as the products are free to escape, or are kept in contact with the wood under increased pressure.

A. Wood exposed to a high temperature in close vessels is converted into charcoal resembling coal and burning with flame. (Hall, *N. Gehl.* 1, 612.) Perfectly dry wood of sycamore, oak, birch, box, or poplar, heated in a sealed glass tube to 360°, melts to a black liquid which solidifies with tumefaction; dry logwood melts to a red liquid which solidifies to a chestnut-brown mass. Wood (even logwood) heated in the same manner with half its weight of water, is converted into a substance resembling bituminous coal, and burning with a smoky flame. (Cagniard Latour.) Wood of the berry-bearing alder dried at 150°, containing 47.51 p. c. C., 6.12 H., 46.29 O., and 0.08 ash, yields, when heated in a sealed glass tube, gases which escape with violence when the tube is opened, a very faintly coloured, clear or milky liquid, and a solid residue, which resembles red coal (*Rothkohle*) if it has been charred between 160° and 200°, black coal (*Schwarzkohle*) between 220° and 280°, and caking coal if charred at still higher temperatures. At 280° it still retains the structure of wood; between 300° and 320° it is tumefied, at 340° fused into a dense mass; it then amounts to 79.1 p. c. of the wood employed, and consists of 77.07 p. c. C., 4.70 H., 14.04 O., and 3.84 ash. (Violette.) The composition of the wood and of the residue at different temperatures, as stated by Violette, are not in accordance with the quantity of the residue. (Ritter.) Vegetable substances strongly pressed between moist clay, so that the vapours can escape but slowly, and heated to between 200° and 300°, yield a residue resembling coal. (Baroulier, *Compt. rend.* 46, 376; *Chem. Centr.* 1858, 363.) Firwood and water heated together in a close vessel to 400°, yielded a coaly residue, black, hard, dense, shining, difficult to burn, and giving off scarcely any traces of volatile matter when heated. (Daubrée, *Ann. Min.* [5], 12, 305.)

B. When wood previously well dried is heated in vessels which allow free egress to the volatile products of decomposition, water is first driven out, and there passes into the receiver, first a colourless, then a yellowish liquid. As the temperature rises, the vapours become smoky, the distillate continually more coloured, and smoky gases escape. The liquid distillate becomes mixed with drops of oil, at first mobile and slightly coloured, then continually more viscid and dark-coloured, so that the exit-tubes are filled with black pitch liquified by the heat. The residue in the retort is charcoal (*Holzkohle*). The liquids which pass over mix in the receiver and separate, when left at rest, into two layers, an upper watery layer, which is *Crude Wood-vinegar*, or *Pyroligneous acid*, and a lower layer consisting of *Wood-tar*.

In the dry distillation of hornbeam-wood (*Carpinus Betulus*), Wöllner's empyreumatic fat is obtained in the outermost receivers, floating on the top of the empyreumatic oil; it resembles mutton-fat, has a specific gravity of 0.979, melts at 94°, and is saponified by alkalis,

yielding glycerin. (Wöllner, *Schw.* 59, 454; *Kastn. Arch.* 1829, 363; *Berzel. Jahresber.* 10, 228.)

The composition of the gaseous, liquid and solid products of the dry distillation depends partly on the constitution of the wood employed, but more on the degree and manner of heating, so that the quantitative proportions of the several compounds vary greatly, and many, under certain circumstances, are absent altogether. At the lower degrees of heat, a comparatively larger quantity of oxygen and hydrogen is employed in the formation of water; at higher temperatures (above  $300^{\circ}$ ) there is a more abundant formation of acetic acid and other oxygen-compounds, together with hydrocarbons; the more rapidly the heat is applied, the larger is the quantity of wood-vinegar and tar produced, and the smaller the quantity of residual charcoal. (Stolze, Winckler, Karsten.)

*Gases.* The gases evolved in the ordinary process of distillation are carbonic oxide, carbonic acid, marsh gas, and hydrogen, containing scarcely any traces of other hydrocarbons; but if wood is heated—as for the preparation of illuminating gas, to a temperature considerably above that at which the liquid products of the distillation are decomposed, olefiant gas and other hydrocarbons of higher atomic weight are formed, at the expense of the tar. (Pettenkofer.)

The crude wood-vinegar and the wood-tar are resolved—according to the kind of treatment to which they are subjected—into various but still mixed products.

a. By distilling off 10 to 15 per cent. of the crude wood-vinegar, *Crude Wood-spirit* is obtained, consisting principally of the more volatile matters such as acetic acid, acetate of ammonia, methylic alcohol, acetate of methyl, lignone, acetone, aldehyde, mesite, pyrocatechin, and pyroxanthogen. It likewise contains, in greater or smaller quantity (probably according to the quantity of the product distilled from the crude wood-vinegar), volatile oils, a substance which turns brown on exposure to the air, and bodies identical with those which remain in larger quantity in the residue of the crude wood-vinegar, and in the tar.

See *Wood-spirit*, vii. 285; *Acetic acid*, viii. 274; *Aldehyde*, viii. 283; [*Scanlan's Liquid*, ix. 55]; *Acetate of Methyl*, viii. 484; [*Acetone*, ix. 1]; *Lignone*, ix. 41; *Mesite*, ix. 53; *Pyroxanthin*, xiv. 163.—The non-bracketed bodies in this list are mentioned in the places cited, with reference to their origin and their separation from crude wood-spirit. Respecting Weidmann and Schweizer's *Mesite* and *Xylite*, see ix. 48; also Völckel (*Pogg.* 83, 272 and 557); on *Creosote* and the *Volatile oils of Wood-spirit*, see below.

On mixing crude French wood-spirit with water, a pale yellow layer of oil separates, which distils over between  $90^{\circ}$  and  $200^{\circ}$ , and may be decomposed by fractional distillation after being treated with oil of vitriol. Toluene, xylene, and cumene are then obtained in succession, and between  $164^{\circ}$  and  $168^{\circ}$ , a peculiar hydrocarbon, isomeric with cumene and mesitylene, but differing from both. (See xiii, 338). (Cahours, *Compt. rend.* 30, 319.)

Pyrocatechin (xi, 379) occurs in crude wood-vinegar to the amount of  $\frac{1}{10}$  to  $\frac{1}{2}$  per cent.,—likewise in all products of the distillation of wood. (Pettenkofer, *Ann. Pharm.* 87, 256; M. Buchner. *Ann. Pharm.* 96, 186).

b. The residual portion of crude wood-vinegar is an aqueous solution

of variable quantities of acetic acid, empyreumatic oil, and resin, and a peculiar extractive matter called empyreumatic extract. (Berzelius.) It likewise contains creosote, a small quantity of eupione, and other volatile oils. (Reichenbach, *comp.* xi, 140.)

By boiling the residue with excess of potash-hydrate, this empyreumatic oil and resin are for the most part removed, while the extract remains dissolved. If the wood-vinegar be neutralised with lead-oxide or ammonia, neutral acetate of lead then throws down the empyreumatic resin, and the filtrate freed from lead by sulphuretted hydrogen, leaves on evaporation, a nitrogenous mass resembling vegetable extract, and separated by alcohol into a soluble and an insoluble portion. The empyreumatic resin still contains acetic acid; it may be further decomposed by digesting it with alcohol, and treating the dissolved portion with ether and soda-ley, and after prolonged boiling with water, is converted into mould-like substances (Berzelius; for further details, see *Berzelius, Lehrb.* 3 Aufl. 4, 499.)

If the distillation of the crude wood-vinegar be continued after the crude wood-spirit has passed over, *distilled wood-vinegar* is obtained, and a red-brown syrup, called *wood-vinegar tar* remains behind. The former, on account of the furfural and creosote which it contains, cannot be obtained colourless, even after repeated rectification, and always leaves a slight residue of wood-vinegar tar. (Völckel.)

The distilled wood-vinegar may be freed by agitation with ether, from volatile oil, creosote, and pyroxanthogen; the former may likewise be removed by neutralisation with potash-ley. On boiling the liquid nearly neutralised with potash-ley, the volatile oils are driven off; and if the residual liquid, while still boiling, be supersaturated with potash, it acquires a deep brown colour, and on subsequent addition of hydrochloric acid, deposits brown flocks, probably produced by decomposition of furfural. By supersaturating distilled vinegar with hydrate of lime, the solution, if immediately filtered, becomes turbid on standing or warming, in consequence of the action of the lime on the volatile oils. On evaporating the liquid, a yellowish brown substance separates, while acetate of lime crystallises out, partly by itself, partly in combination with Völckel's assamar.

The wood-vinegar tar mixed with water deposits a black-brown viscid mass, the supernatant liquid remaining strongly coloured. If the viscid mass be freed by repeated boiling with water from adhering acetic acid, Völckel's assamar, creosote and volatile oils, the residue becomes bitter and friable, and yields to ether a red-brown resin (softening by heat, having a pitchy odour, which it loses by prolonged heating to 100°, solidifying at the same time,—and containing 70·36 p. c. C., 7·4 H., and 22·24 O.);—it afterwards yields to alcohol a brown substance (containing 63·9 p. c. C., 5·1 H., and 31·0 O.), a small quantity only remaining undissolved. This body soluble in alcohol is, according to Völckel, produced from his assamar by elimination of water and formic acid. (Völckel.)

e. If the wood-tar be again subjected to distillation, three layers of liquid collect in the receiver, the upper being *light tar-oil* (the *empyreumatic oil* of Berzelius), the middle consisting of wood-vinegar and water, and the lowest, of *heavy tar-oil* (the empyreumatic resin and oil of Berzelius.) When about half the tar has been distilled off, the residue solidifies on cooling, forming the *black pitch* of commerce.—If the

entire distillate be again rectified, the liquid which passes over consists chiefly of eupione, so long as it floats on the water, afterwards of creosote when it sinks, and finally of paraffin, when grey vapours make their appearance. (Reichenbach.) After the paraffin, chrysene and pyrene ( $C^{20}H^{12}$ ) pass over. (Laurent.)

The usual constituents of wood-tar are the following, besides small quantities of those which pass over in greater quantity into the crude wood-spirit and wood-vinegar, mesite (ix, 53), toluene (xii, 226), xylene (xiii, 116), cumene (xiii, 338), methol (xiii, 341), and a peculiar hydrocarbon isomeric with cumene (xiii, 341); eupione (*vid. inf.*), creosote (xi, 134), carbolic acid, cresol, capnomor, picamar, pittacal, cedriret, paraffin, naphthalin, paranaphthalin, chrysene and pyrene.

The heavy tar-oil obtained in the distillation of very resinous woods contains retene  $C^{26}H^{18}$  (Krauss & Fehling; Fritzsche.)

The first portions of empyreumatic oil obtained in the distillation of wood are colourless and mobile, but the subsequent portions are yellow, finally brown and black, and at the same time more viscid. On rectifying this oil *per se*, the same appearances are repeated, and charcoal is left in the retort at each distillation. But by distilling the empyreumatic oil, a few times with water, it is obtained colourless and mobile, and leaves a residue of pitch. (Berzelius, *Lehrb.* 3 Aufl. 8, 486.) The residue left on distilling the empyreumatic oil with water, yields to water, acetic acid and resin, while a resin is left, identical with that obtained from glance-soot (*Glanzruss*). (Colin, *Ann. Chim. Phys.* 12, 209.)

The first twenty litres of the volatile distillate from 600 kilogrammes of beechwood tar contain acid water and mesite, together with smaller quantities of creosote, eupione, and picamar. The picamar may be prepared from that portion of the distillate whose specific gravity lies between 0.9 and 1.15; the pittacal and capnomor from that portion of the tar obtained in the course of the distillation which sinks in water. (Reichenbach; for further details respecting this body see below.)

*Light Tar-oil.*—This oil always passes over yellow, even after repeated distillation, because it contains furfurol, pyroxanthogen, and other substances. When subjected to dry distillation, it yields, between  $40^{\circ}$  and  $100^{\circ}$ , a small quantity of liquid, consisting of acetate of methyl, acetone, mesite, xylite, and products of decomposition of the latter bodies; and between  $100^{\circ}$  and  $200^{\circ}$ , a mixture of oxygenated and non-oxygenated products. The portion which goes over between  $100^{\circ}$  and  $150^{\circ}$ , yields, when treated as directed at page 341, vol. xiii., toluene, xylene, oxide of mesityl, and a small quantity of methol; the distillate obtained between  $150^{\circ}$  and  $200^{\circ}$ , yields, when treated in like manner, methol and oxide of mesityl, and appears to contain a small quantity of capnomor. (Völckel, *Ann. Pharm.* 86, 331.) The light volatile tar-oil appears, therefore, partly to go over with the wood-spirit, inasmuch as Cahours found the same bodies in French wood-spirit (see page 150). The volatile oil from wood-spirit examined by Kane (*Ann. Pharm.* 19, 168), was doubtless also a mixture of the same bodies (Kr).

*Reichenbach's Eupione.*—Under this denomination, Reichenbach described several bodies, probably of mixed nature. Subsequently the name was applied to certain empyreumatic oils, agreeing with Reichenbach's eupione in being unalterable by oil of vitriol or by potash-ley

(xiv, 324). (Gregory, *J. pr. Chem.* 4, 5.—R. Brandes, *N. Br. Arch.* 16, 122.)—*a. Formerly* (*Schw.* 61, 177; 62, 129; *Berz. Jahresber.* 12, 309), Reichenbach obtained eupione from wood-tar, or from the tar of animal substances,—by freeing the light tar-oil from all its alterable constituents by agitation with oil of vitriol, distillation with nitre and oil of vitriol, and digestion with potash-ley, oil of vitriol, and hot potash-ley successively,—and then rectifying the floating eupione over potassium,—as a colourless, thin, tasteless, and odourless liquid, of sp. gr. 0.74, boiling at 169°, not solidifying at 20°, difficult to set on fire, but burning from a wick with a smokeless flame. This eupione is regarded by Völckel (*Pogg.* 82, 496) as a mixture of the hydrocarbons from light tar-oil.—*b. More recently* (*J. pr. Chem.* 1, 377; *Berz. Jahresber.* 15, 400), Reichenbach prepares eupione from the oils obtained by the dry distillation of rape-oil, in the same manner as formerly from wood-tar, and now obtains it as a colourless, extremely mobile liquid, of high dispersive power, of sp. gr. 0.655 at 20°, and boiling at 47°.—Eupione prepared by Reichenbach did not boil when immersed in water at 80°, and contained 77.46 p. c. C., 14.31 H., and 8.23 O. (Hess, *Ann. Pharm.* 23, 253).—From birch-wood tar, Hess (*Pogg.* 36, 417) obtained by Reichenbach's method, only the heavy volatile eupione boiling between 100° and 140°, and containing equal numbers of atoms of carbon and hydrogen; but from oil-tar he obtained a very mobile liquid, which passed over between 45° and 75°, and was not altered by oil of vitriol. The latter still contained oxygen, and after deducting this element, it contained carbon and hydrogen in the atomic proportion  $C^{10}H^{12}$ ; according to Frankland (*Ann. Pharm.* 74, 57), it is perhaps partly or wholly identical with hydride of amyl  $C^{10}H^{12}$ .

By repeated fractional distillation of the *heavy tar-oil*, a light oil which passes over at the beginning of the distillation, and paraffin which passes over at the end, may still be separated. When enough carbonate of potash to neutralise the acetic acid which still adheres to it, is added to the middle portion, an oil separates, which may be divided, by agitation with potash-ley of sp. gr. 1.2, into an insoluble part (which contains light volatile oil) and an alkaline solution, from which acids separate creosote and capnomor.—The portion of pine-wood tar which distils between 150° and 220°, contains carbolic acid and cresylic alcohol. (Duclos, *Ann. Pharm.* 109, 135). Gorup-Besanez could not detect carbolic acid in beech-wood tar. (*Ann. Pharm.* 87, 258).

*Black pitch* dissolves almost completely in alcohol and in potash-ley. When its alkaline solution is boiled, a coloured oil, possessing a stupefying smell passes over; and when made acid again, it yields volatile fatty acids on boiling, while a black mass is deposited. On boiling this mass with water, creosote is given off; and if the treatment with potash and acid, which has just been described, be several times repeated, the black mass is converted into a black powder, which, after long boiling with hydrochloric acid, yields to alcohol only a small quantity of resin, and there remains a substance, insoluble in alcohol and also in potash, and containing 65.04 p. c. carbon, 4.89 p. c. hydrogen, and 30.07 p. c. oxygen. (Völckel.)

The residue left by the destructive distillation of wood,—the *charcoal*, that is,—retains the structure and form of the wood but has a smaller bulk. Between 280° and 340°, it is obtained as *red coal*, and at higher temperatures as *black coal* (comp. p. 149); the more

intense the heat, the less hydrogen and oxygen does it retain, but it is not obtained quite free from them, even if heated to the melting point of platinum. The specific gravity, hardness, and conducting power of charcoal, increase with the temperature at which it is prepared; its absorptive power for water, and its inflammability, on the other hand, diminish as the temperature rises. Charcoal prepared at  $290^{\circ}$  has sp. gr. 1.406, that prepared at the melting point of platinum has sp. gr. 2.002; prepared at  $260^{\circ}$ — $280^{\circ}$ , it takes fire in the air at  $340^{\circ}$ — $360^{\circ}$ ; prepared at the melting point of platinum, it does not take fire below the melting point of copper. The employment of overheated steam renders the charring more uniform, and causes it to take place at a lower temperature than it otherwise would. Charcoal prepared by means of overheated steam, below the melting point of antimony ( $430^{\circ}$ ), has the properties of charcoal prepared without steam, at  $1200^{\circ}$ . (Violette.)

The products of the distillation of *peat*, *lignite*, and *coal*, contain a large proportion of the compounds obtained by distilling wood; the more recent the formation of the substance employed, the more of them does the distillate contain. Light, pale-coloured peat and lignite, which still show a distinctly woody structure, yield a light tar, and an acid watery distillate, often in such quantity that the latter might be employed for the manufacture of wood-vinegar; while heavy, dark, black peat and most kinds of lignite, yield ammonia-water, and a heavy tar containing volatile bases. Peat begins to decompose at  $109^{\circ}$ , yielding at first water and a small quantity of yellow, mobile oil, and afterwards ammonia-water and tar. The various kinds of peat yield 5.6 to 9.2 p. c. tar, and 25 to 39 p. c. ammonia-water. Lignite is decomposed much below red heat and yields 1.5 to 12.75 p. c. tar and 12 to 70 p. c. ammonia-water. Peat- or lignite-tar is coffee-brown, of sp. gr. 0.880—0.975, and generally solidifies, from containing paraffin, when cooled. In the further treatment of the tar, it is carefully freed from ammonia-water by being heated to  $100^{\circ}$  and allowed to subside; the heavier tars are slowly heated, common salt or Glauber's salt being added to hasten the separation; and then the tar alone is gradually heated in a still. Gaseous sulphide of ammonium and pyrrol-bases pass over below  $100^{\circ}$ ; at  $100^{\circ}$ , a little very strong ammonia-water and light oil of sp. gr. 0.700; next follow oils of constantly increasing density in accordance with which they are separated into various portions. Above  $200^{\circ}$ , a fresh quantity of water appears, separated out from carbolic acid and creosote, and, when the water has ceased to come, oils containing paraffin. The distillation is continued till the residual asphalt-pitch has acquired the proper degree of hardness, or until it is entirely charred. (Vohl.) Vohl thus obtained from many different peat-tars, from 11 to 34.6 p. c. light oil of sp. gr. 0.820, from 8.67 to 36 p. c. heavy oil of sp. gr. 0.860, from 0.424 to 8.01 p. c. paraffin, and from 11.54 to 42.4 p. c. asphalt-pitch; from lignite-tars, he obtained from 10.63 to 33.5 p. c. light oil, from 11.11 to 43.6 p. c. heavy oil, from 1.25 to 6.73 p. c. paraffin, and from 11.11 to 22.22 p. c. pitch. From other peat-tars, he obtained 18.9—34.5 p. c. carbolic acid and creosote, and 46.5 p. c. from lignite tars. The gas evolved at the beginning of the distillation of peat has little or no luminosity; later on, as the temperature rises, it has somewhat more. In order to use peat or lignite for the preparation of illuminating gas, they must be treated in the same way as wood. Coal-tar is specifically heavier than the foregoing,—its sp. gr. is 1.12—1.15 (Mansfield),—richer in volatile

bases, heavy oils, and generally in naphthalin; as the last product, however, is only produced by the contact of the vapours with the red-hot sides of the retort (see xiv. 2, 3) it is not a necessary constituent, and may be entirely wanting in tar which distils at a comparatively low temperature. It is generally found in coal-tar, and in larger quantity when clay retorts are used than when iron retorts are employed. The more naphthalin a tar contains, the less paraffin can be found in it. Grace Calvert found in tar from Boghead-coal, 41 p. c. paraffin but no naphthalin, and, on the other hand, in tar from three other kinds of coal, no paraffin, but as much as 58 p. c. naphthalin. These tars contained 3 — 14 p. c. carbolic acid, 2 — 12 p. c. light oil, 12—35 p. c. heavy oil, and 14—29 p. c. pitch. Thenius found in gas-tar, on an average, 4 p. c. light oil, 3 p. c. pure carbolic acid, and 4 p. c. ammonia-water; on the contrary, he found, in tar obtained by careful destructive distillation, more than 30 p. c. of light oil of sp. gr. 0.900. The further treatment of coal-tar on the large scale for the purpose of obtaining its several constituents, is the same as that followed in the case of peat and lignite-tar. For the mode of separating the various hydrocarbons, see xi. 135 — 137; for the mode of separating the carbolic acid see xi. 143.

In addition to the substances already enumerated as contained in wood-tar, coal-tar contains rosolic and brunolic acids (Runge), propyl ( $C^3H^4$ ), butyl ( $C^4H^6$ ), amyl ( $C^5H^{10}$ ), and caproyl ( $C^6H^{12}$ ),—[¶ according to Williams's latest experiments, (*Chem. Soc. J.* 15, 130) these hydrocarbons, which he formerly believed to be homologues of methyl and ethyl, are probably homologues of marsh-gas (hydride of methyl); *e. g.*,  $C^{12}H^{14} = C^{12}H^{13}, H$  (hydride of caproyl),  $C^{16}H^{18} = C^{16}H^{17}, H$  (hydride of capryl) &c. ¶],—caproene, cœnanthylene (Williams), parabenzene (Church), cymene (Mansfield), methylamine and its homologues up to amylamine (Williams), aniline (Runge, Hofmann), pyridine, picoline, lutidine, collidine, parvoline (Williams), corridine ( $C^{20}NH^{16}$ ), rubidine ( $C^{22}NH^{17}$ ), viridine ( $C^{24}NH^{19}$ ), (Thenius), chinoline, lepidine, cryptidine, (Williams), pyrrol (Runge),<sup>†</sup> anthracene ( $C^{14}H^{10}$ ) (Laurent, Anderson). The bases are combined with hydrosulphuric, acetic, carbonic, prussic, and hydro-sulphocyanic acids, and, in the watery distillate and tar from lignite and peat, with formic, propionic, and butyric acids (Sullivan), and valerianic acid. (Vohl.)

Many of these bodies are probably also contained in wood-tar, and have not as yet been found in it, only because they exist in too small quantity.

The liquid hydrocarbons, with the exception of cymene which passes into the heavy oil, are found for the most part in the light coal-tar-oil. The boiling points of several of them lying very close together, it is impossible to separate them by fractional distillation; hence, according to Anderson, the following process must be followed for this purpose. The hydrocarbons of the general formula  $C^nH^n$  are converted into bromine-compounds by agitation of the mixture with bromine and water; the hydrocarbons  $C^nH^{n+2}$  and those of the benzene series,  $C^nH^{n-6}$ , which remain unaffected by this treatment, are distilled off; the residue left to stand, and the middle layer of the three into which it separates repeatedly distilled with alcoholic potash and sodium, in order to reproduce the hydrocarbons  $C^nH^n$ . In this way, caproene, b. p.  $71^\circ$  (see xi. 411. The boiling point of caproene is  $55^\circ$  according to Fremy [W]),—may be obtained from that portion of the distillate from Boghead-coal which



passes over between  $71^{\circ}$  and  $77^{\circ}$  and has sp. gr. 0.75, and cenanthylene, b.p.  $99^{\circ}$  (xii. 445), from the portion which boils between  $82^{\circ}$  and  $88^{\circ}$ . (Anderson.) The liquid distilled off from the bromine-compounds is treated with fuming nitric acid, or with nitro-sulphuric acid, whereby the hydrocarbons of the general formula  $C^nH^{n-6}$  are converted into nitro-compounds; the portion not attacked by the acids is separated, washed with aqueous alkali, dried by means of solid potash, and rectified over sodium: by this process a mixture of hydrocarbons isomeric with the alcohol-radicals is obtained, the constituents of which can be separated from one another by fractional distillation. (Anderson.) Carbolic, rosolic, and brunolic acids occur principally in the heavy oil, and naphthalin also to some extent; but the last substance is chiefly obtained, together with paranaphthalin, chrysene, and pyrene, by the distillation of the pitch. The volatile bases occur, according to Hofmann, for the most part (to the extent of about 1 p.c.) in the heavy oil: according to Thenius, in the light oil of sp. gr. 0.890 — 0.900: and the bases of the chinoline series, according to Williams, in the heaviest oil. Pyrrol and adhering hydrocarbons are removed by boiling from the acid solution of the crude bases, obtained by shaking the oil with sulphuric or hydrochloric acid after it has been strongly cooled to separate the naphthalin; the bases are then separated by caustic potash, purified by being several times alternately dissolved in acid and separated by alkali, dried by distillation over solid potash, and the several bases are at last separated from each other either by fractional distillation, or, according to Williams, by fractional distillation and by fractional crystallisation of their platinum-salts. According to Anderson (*N. Phil. Mag. J.* 9, 214, 214), aniline cannot be separated by distillation from the bases of the pyridine series; in order therefore to prepare these in a state of purity, the aniline must be previously destroyed by nitric acid. For the preparation of the individual bases from coal-tar, see xi. 247, 264; xii. 337; xiii. 149, 245; xiv. 103, 519; xv. 5.

The acids of the fatty acid series, together with hydrocyanic, hydrosulpho-cyanic, and hydrosulphuric acids, are found principally in the ammonia-water, in combination with ammonia, methylamine, and other bases. The several constituents are not, however, strictly separated from each other according to the principal subdivisions of the products of distillation, but are for the most part contained, though only in small quantity, in each of them.

The distillation of coal being commenced at a temperature at which a part of the liquid products of distillation are decomposed, the gas so formed always contains from the beginning luminous hydro-carbons; towards the end, when the heat is much increased, scarcely anything is formed but marsh-gas and hydrogen, and at last the latter gas only. Coal-gas generally contains sulphide of carbon vapour. The residue of the distillation, the coke, varies in its properties in the same way as charcoal, according to the degree of heat employed.

2. *By the action of the air.*—A. Wood either dry or moist inclosed with air, forms carbonic acid in the course of a few months at the ordinary temperature. (Karsten, *Berl. Acad. Ber.* 1860, 38; abstr. *J. pr. Chem.* 79, 226).

B. The sawdust of recently felled timber (oak and hornbeam), pressed together and kept in a moderately warm place, enters after some time into vinous fermentation (caused by the presence of sugar

and albuminous substances in the sap), and yields an alcoholic distillate. (Chevandier.)

C. In moist air, wood decays or moulders; whereby a distinction is made between dry-rot and wet rot. When undergoing dry-rot, which occurs when it is moderately damp and air is almost excluded, wood retains its light colour, and often even becomes lighter, and its elements separate in almost the same proportions as those in which they exist in wood. Dry-rot is sometimes accompanied by evolution of light. (i, 191). It is always accompanied by a fungoid growth, but whether as cause or effect cannot be decided. In wet rot, mouldering (simultaneous decay and putrefaction), wood assumes continually a darker and darker colour, and becomes continually richer in carbon, mould being produced at the same time. Moist wood, putrefying in confined air changes the oxygen of the air into carbonic acid, but produces even more water than carbonic acid. (Saussure.) Decaying vegetable substances putrefy in an atmosphere of hydrogen, but continue to evolve carbonic acid (Saussure); hence Liebig assumes that the formation of carbonic acid during decay is due to the oxygen of the substance, and that the oxygen of the air unites with the hydrogen of the body undergoing decay. From Mayer's and Will's analyses of oak-wood mould, and from Gay-Lussac & Thénard's analyses of oak-wood, he concludes that 1 at. carbonic acid is formed for every atom of water. — Hermann found 186.3 volumes of air, with which 21 volumes of putrefying wood had been in contact for five days, diminished by 4.3 volumes, 3.5 vols. nitrogen and 27.8 vols. oxygen having been replaced by 27.0 vols. carbonic acid. In 262 vols. of air, 13 vols. nitrogen and 27 vols. oxygen were replaced by 40 vols. carbonic acid after ten days contact with 28 vols. rotting (not completely rotten) wood. By making the arbitrary assumption that, in the last case, the water with which the wood was moistened, absorbed "about" 13 vols. carbonic acid, Hermann concluded from these experiments, that, in the production of mould, nitrogen is taken up from the air and nitrogenous mould and ammonia formed, and that, in the decay of fresh wood, 4 measures of carbonic acid are formed for every 1 measure of nitrogen and 2 measures of oxygen. (Since, however, the air contained in the rotting wood, which contains, according to Dessaignes (i. 192), a great deal of carbonic acid but only a little oxygen, is not taken into account here, it is more likely that the differences in the proportion of nitrogen in the air are caused by the exchange of nitrogen for carbonic acid existing ready formed in the wood: Ritter.) He assumes the formula  $C^{36}H^{22}O^{22}$  to represent the composition of wood, and expresses its decompositions during putrefaction by the following equations:

a.  $C^{36}H^{22}O^{22} + O^4 + N = 4 CO^2 + 4 HO + C^{32}NH^{16}O^{14}$  (Nitrolin).

b. Further decomposition of the nitrolin:  $5 C^{32}NH^{16}O^{14} + O^{52} + N^{35} = C^{70}N^{35}H^{35}O^{23}$  (Holzhumussäure) +  $2 C^{32}NH^{16}O^{14}$  (Humusextract) +  $3 NH^3 + 26 CO^2 + 14 HO$ ;

or,  $4 C^{32}NH^{16}O^{14} + O^{50} + N^{35} = C^{70}N^{35}H^{35}O^{23}$  (Holzhumussäure) +  $C^{32}NH^{16}O^{14}$  (Humusextract) +  $3 NH^3 + 26 CO^2 + 12 HO$ .

He supposes that 1 at. of the ammonia thus formed remains combined with the "Holzhumussäure," and that 2 at. volatilise.

c. Further decomposition of "Holzhumussäure:"  $6 C^{70}N^{35}H^{35}O^{23} + O^9 + N^{35} = 5 C^{18}NH^6O^9$  (Humusquellsäure) +  $11 C^{30}N^{15}H^{15}O^9 + 33 HO$ ;

d. "Torfsatzsäure."  $C^{30}N^{1.5}H^{12}O^9 + 12HO + O^3 + N^{0.5} = 2C^{15}NH^{12}O^{12}$ . Mulder assumes the existence from the first in rotting wood, of crenic acid,  $C^{24}H^{12}O^{16}$ ; apocrenic acid,  $C^{48}H^{12}O^{24}$ , and ulmic acid,  $C^{40}H^{14}O^{12}$ , the first of which disappears when air has free access. He assumes that, in general, oxygen is thereby absorbed from the air, but that only a little carbonic acid is formed. This applies especially to the incrusting substance; in the case of cellulose ( $C^{24}H^{21}O^{21}$ , according to Mulder) he supposes a simple splitting up, without absorption of oxygen; thus,  $2 C^{24}H^{21}O^{21} = C^{40}H^{14}O^{12}$  (ulmic acid) +  $8 CO^2 + 14 HO + H^{14}$ ; or,  $5 C^{24}H^{21}O^{21} = C^{40}H^{14}O^{12}$  (ulmic acid) +  $C^{24}H^{12}O^{16}$  (crenic acid) +  $C^{48}H^{12}O^{24}$  (apocrenic acid) +  $8 CO^2 + 37 HO + H^{30}$ . Hence, and from the processes which he supposes to take place in the further oxidation of the constituents of mould to carbonic acid (e. g.,  $C^{40}H^{14}O^{12} + C^{24}H^{12}O^{16} + C^{48}H^{12}O^{24} + O^{17.2} = 112 CO^2 + 38 H$ ), he assumes that probably in most cases a large excess of hydrogen remains, and supposes that it is not wholly oxidised by the air; and that, when air has only partial access, carbonic oxide and carburetted hydrogen are formed instead of carbonic acid, the excess of hydrogen uniting with nitrogen from the air to form ammonia. He seeks to support this view by the observation that mould, as it occurs in nature, always contains ammonia, and by the experiments already quoted (vii, 94), in which he left substances free from nitrogen in contact either with air or water only, or with air, water, and charcoal, and so obtained ammonia or (nitrogenous) mould. The yield of ammonia in these experiments, seems to have been greater in proportion as the raw material, from which the non-nitrogenous substance was prepared, was richer in nitrogen. Cane-sugar yielded but little, milk-sugar much more, while starch acquired a distinct smell of cheese, and evolved gas.

D. When the supply of air is very limited, as under water containing air, the decay of wood assumes still more the character of putrefaction. Carbonic acid and marsh-gas are evolved, and the formation of peat (principally from the lower marsh-plants mixed with only occasional woody particles), of lignite (*brown coal*), and (after a very long time) of coal, takes place, accompanied by a fungoid growth, mostly of an acid character. Many kinds of lignite contain hydrogen and oxygen in the proportion to form water. The lignite of Ringkuhl has been formed from oak-wood by the loss of carbonic acid and water. (Liebig.)—Assuming that heat and pressure have not exerted an influence, and that atmospheric oxygen has not had access, the formation of lignite must have been accompanied by absorption of oxygen and evolution of carbonic acid, marsh-gas, and water. (Bischoff, *J. pr. Chem.* 31, 329.) The piles of ancient bridges are sometimes almost entirely converted by river-water into a brown, easily powdered mass. (Hervé-Mangon, *Bull. Soc. d'Encouragement*, 1857, 634.) Apparently well preserved wood from an ancient fortification on the sea-coast, near Carthage, contained 58.9 p. c. ash and 31.6 p. c. organic matter, consisting, when dried at  $120^\circ$ , of 58.9 — 60.0 p. c. C., 5.8 — 5.9 p. c. H., 0.6 p. c. N., and 33.5 — 35.0 p. c. O., and therefore approximating to the composition of lignite. (Péligot, *Compt. rend.* 44, 933.)—Elevation of temperature may produce the same result as length of time in decay of this kind. Wood and plants heated in water, with access of air, to  $100^\circ$  in the day-time and to  $62^\circ$  —  $75^\circ$  at night, during 1 — 2 years, were converted into lignite, but not into

coal even after  $2\frac{1}{2}$  years' heating. With the addition of a quantity of green vitriol, equal to 1 p. c. of the vegetable matter, they became like coal. (Göppert, *Pogg.* 72, 174; *J. pr. Chem.* 42, 56.) Concerning the preservation of Wood see vii, 112.

3. *Action of the air at high temperatures.*—A. With limited access of air: *Charcoal-burning, Distillation of Tar, Manufacture of Lamp-black.* These processes are essentially the same as dry distillation, the only difference being that, instead of heat being applied externally, it is generated by the partial combustion of the substance operated upon. The products are therefore nearly the same. In charcoal-burning, the vapour is not condensed. In the manufacture of lamp-black it is decomposed, partly by more air being allowed to have access, partly by exposure to a high temperature in a flue of masonry which very soon becomes red-hot, in such a way that almost all the hydrogen is burnt, and nothing remains but finely divided carbon mixed with naphthalin and small quantities of ammonia and of a substance resembling mould.

Concerning the empyreumatic oil obtained in the distillation of tar see p. 151.

Soot contains many salts, chiefly carbonates, muriates, sulphates, phosphates, and acetates of ammonia, potash, lime, and magnesia. It yields to water 56 p. c. of soluble matter, and from the residue 18.5 p. c. of ulmin can be extracted by alkalis. The aqueous solution also contains ulmin. When evaporated to an extract, ether, employed either alone or with addition of hydrochloric acid, takes up from it a light yellow, bitter oil, which dissolves in a large quantity of water, and is precipitated from its aqueous solution by sugar of lead, at first with a yellow, afterwards with a green colour, and is also precipitated by tincture of galls, and is further soluble in alcohol, but not in oil of turpentine, and is decomposed by heat or by nitric acid. This substance is Braconnot's *Asbolin*. When the aqueous solution of soot is precipitated by sugar of lead, and the liquid evaporated to the consistence of honey after the excess of lead has been removed by sulphuretted hydrogen, alcohol precipitates from the residue Braconnot's *animal matter of soot*. This body deposits reddish-yellow, transparent scales by solution in water and evaporation, and yields empyreumatic oil and carbonate of ammonia by destructive distillation. (Braconnot, *Ann. Chim. Phys.* 31, 37, & 53.) Lamp-black also contains many salts and a resin resembling asphalt, which can be extracted by oil of turpentine, and further broken up by alcohol. (Braconnot.) By distillation, either alone or with water, it yields empyreumatic oil and naphthalin; the latter body is also found sublimed inside the lids of the casks in which lamp-black is kept. (Reichenbach, *Schw.* 61, 188.) Acids give, in the alkaline extract of soot, a precipitate which, after being dried at  $140^{\circ}$ , boiled with alcohol, and again dried at  $140^{\circ}$ , still contains naphthalin, which must therefore exist chemically combined with ammonia and humic acid. (Mulder, *J. pr. Chem.* 21, 331.) Glance-soot (a compact carbonaceous deposit which collects in flues where wood is burned) is only slightly soluble in alcohol, but dissolves easily in soda-ley, giving a solution which becomes gelatinous. (Mac Cullock, *Edinb. J. of Sc.* 1, 321.)

B. With free access of air, wood burns with a luminous flame, the gases and vapours generated by the heat of the combustion itself being immediately and completely burnt without smoke when the air

is renewed with sufficient rapidity, but with production of smoke when the air is not quickly enough renewed. The smoke condenses in the chimneys of the fire-places to glance-soot, which contains the ingredients mentioned in the case of lamp-black but in larger proportions. Concerning Hünefeld's *acid of carbon-vapour* (Kohlendunstäure) See *J. pr. Chem.* 7, 29.

4. Deal sawdust did not change colour when kept several years in *water* free from air. (Saussure. *Ann. Pharm.* 42, 276) — 5. *Chlorine* attacks principally the incrusting substance: the cellulose of wood it attacks but slightly or not at all. (Payen; comp. *Cellulose* p. 134.) — 6. Wood is blackened by contact with *oil of vitriol* (pp. 136—138) — 7. By concentrated *nitric acid*, it is converted without change of form into substances resembling pyroxylin (p. 135) which explode by heat; it is coloured yellow or brown according to the quantity of foreign substances mixed with it. Nitric acid extracts colouring matter from ebony-wood without injuring its tissue. (Dutrochet). Oak, fir- and pine-wood became gelatinous by lying four days in fuming nitric acid; when afterwards washed with aqueous ammonia, they became yellow, and again colourless when washed with water; under the microscope they exhibited a cellular structure, and, after being boiled out with alcohol, they had the composition of cellulose (43.72 to 44.20 p. c. C., 5.92 to 5.99 p. c. H., 49.84 to 50.36 O.). No xyloidin is thus formed. (Mulder.) — Deal sawdust, dried at 100°, yields oxalic and pectic acids when boiled with 2 pts. water and 5 pts. nitric acid. (Sacc, *N. Ann. Chim. Phys.* 25, 218; *J. pr. Chem.* 46, 360). Concerning Sacc's pectic acid see below.

8. When treated with aqueous *alkalis*, wood becomes less rich in carbon, because incrusting matter is removed and cellulose remains in a state of greater or less purity. (Payen.) (Comp. *Cellulose* p. 144, Frémy.) — Sawdust gives oxalic acid and hydrogen by the action of fused potash, in the same way as cellulose. (Gay-Lussac, *N. Ann. Chim. Phys.* 41, 398; *Pogg.* 17, 171.) — When evaporated to dryness with equal quantities of potash and water, almost the whole quantity of wood is dissolved and converted into ulmin at the instant of frothing up (Bräconnot); the whole quantity of wood remains almost always unaltered. (Schleiden, *Ann. Pharm.* 42, 302.)

9. In the manufacture of white lead by the Dutch process (v. 124), the boards which are exposed to the action of the air, carbonic acid, aqueous vapour, acetic acid, and ammonia at an elevated temperature, become, after being used 8 or 10 times, each time for 30 to 40 days, brown or black, light, crumbly, burn almost without flame, and contain a large quantity of ammonia and other salts, together with mould. (Payen, *N. Ann. Chim. Phys.* 16, 231.) — 10. Wood exposed to the action of water, particularly of sea-water, in contact with iron and air, becomes at first black, from the formation of a compound of ferros-ferric oxide, and soon afterwards, the ferric oxide acting as a carrier of oxygen, crumbly and pulverisable; hence iron nails cannot be used in shipbuilding. (Kuhlmann.)

#### *Interpolation.*

1. *Cedriret*. Obtained from beech-wood tar-oil. The oil is freed from acetic acid by neutralisation with carbonate of potash, mixed

with concentrated potash-ley, the oil which swims on the top of the ley removed, and the ley neutralised with acetic acid. Part of the dissolved oil is thus separated out, while another part remains in combination with the acetate of potash, from which it may be obtained by distillation. As soon as a drop of the distillate gives a red precipitate with aqueous ferric sulphate, the remainder is collected apart. When treated with ferric sulphate or with bichromate of potash and tartaric acid, this portion becomes red, and, on standing, deposits red needles of cediret. — Thin red needles, which decompose when heated, without melting. *Inflammable*, burning away without residue. Dissolves in oil of vitriol with indigo-blue colour, which becomes yellow-brown by heat or dilution. — Decomposed by concentrated, not by dilute nitric acid. — Slightly soluble in boiling acetic acid, not precipitable by ammonia. Soluble with purple colour in creosote, precipitated crystalline by alcohol; not soluble in other solvents. (Reichenbach, *Berzel. Jahresb.* 15, 408.) Völckel (*Ann. Pharm.* 86, 102) did not succeed in obtaining Reichenbach's cediret.

2. *Creosote*. Appendix to vol. xi, page 139. — Hlasiwetz & Barth obtained, by fractional distillation in a stream of hydrogen, a creosote which distilled between 205° and 210°, and contained 74.57 p. c. C., 8.09 p. c. H., and 17.34 p. c. O. It consists, according to them, of a compound called *creosol*,  $C^{16}H^{10}O^4$ , since it gives, when treated with potassium in a stream of hydrogen, compounds containing  $O^{18}KH^9O^4$  and  $C^{32}KH^{18}O^8$  (and bodies of similar composition when treated with ammonia, hydrate of baryta, bromine, and other bodies) and at the same time a second substance, not yet isolated. When treated with potassium, it yields by evaporation a small quantity of a colourless oil which is more fluid than creosote, no longer becomes solid with potash-hydrate, distils for the most part between 193° and 195°, and contains on an average 75.4 p. c. C., and 8.8 p. c. H., but which still indicates the presence of creosote when tested with alcoholic ferric chloride. The products obtained from creosote by distillation with lime, or by long boiling with potash, are probably, according to them, mixtures resulting from the decomposition of the creosote and of the second constituent. (Hlasiwetz, *Ann. Pharm.* 106, 339: for details see the original paper.)

3. *Capnomor*. — When heavy beech-wood tar-oil is agitated, as for the preparation of creosote, with potash-ley of sp. gr. 1.20, capnomor dissolves together with the creosote. The insoluble oil floating on the surface is removed; the alkaline solution is boiled for some time, cooled, and supersaturated with sulphuric acid; and the dark-brown oil which separates is distilled after the addition of a little caustic potash; the distillate is shaken up with potash-ley of sp. gr. 1.16; the undissolved portion removed; and the alkaline solution boiled, cooled, treated with sulphuric acid; and the mixture of creosote and capnomor, which separates, is distilled as before. The same treatment is repeated three times more with the product, but each time more dilute potash-ley is used, viz.: first of sp. gr. 1.12, then of sp. gr. 1.08, and lastly of sp. gr. 1.05. The undissolved oils all contain capnomor, but the portion which remained undissolved when treated with the dilutest potash-ley contains the most. This is accordingly mixed with an equal quantity of oil of vitriol (whereby it is heated and coloured red), and, when cold, diluted with water; it is freed from the oil which swims on the surface, and then neutralised with ammonia. The oil which thus

separates is also removed, and the clear liquid distilled; capnomor then passes over towards the end of the distillation, and is again dissolved in sulphuric acid, the solution diluted with water, neutralised with ammonia, and redistilled. The product thus obtained is washed with potash-ley and rectified, the portion which passes over below  $185^{\circ}$  and whose specific gravity does not exceed 0.98, being collected. — Colourless oil, refracts light strongly, has an agreeable aromatic smell; sp. gr. 0.9775, at  $20^{\circ}$ ; boiling point,  $185^{\circ}$ . Neutral. Burns with a smokeless flame; permanent in the air; not affected by boiling with red lead, oxide of copper, or mercuric oxide, but reduces permanganic acid, acetate of silver, and terchloride of gold, the last to the metallic state. — Decomposed by bromine and chlorine; coloured green and then brown by nitric acid of sp. gr. 1.45; decomposed, when heated with strong nitric acid, with formation of oxalic and picric acids and peculiar crystals. — Coloured purple-red by oil of vitriol of sp. gr. 1.85; black, by hot oil of vitriol. Water or aqueous alkalis do not separate any capnomor from the purple-red solution; but, the acid solution partially saturated with potash, deposits a combination of capnomor with acid sulphate of potash, which dissolves again on heating, and crystallises by cooling in cauliflower-like shapes, and does not yield any capnomor to alcohol. — Capnomor is but little changed by potassium or sodium. It dissolves several salts, several alkaloids, and many other vegetable substances; it causes caoutchouc to swell up, and dissolves it with the aid of heat. — It dissolves in 300 pts. of boiling glacial acetic acid, and in all proportions in alcohol, ether, acetic ether, acetone, fusel oil, oil of turpentine, and creosote. (Reichenbach, *J. pr. Chem.* 1, 1; *Berzel. Jahresh.* 15, 402.) According to Völckel, Reichenbach's capnomor does not exist ready formed in tar-oil, but is produced during the treatment with sulphuric acid. Völckel, obtains his capnomor [which, however, Gorup-Besanez (xi, 142, 145, 149) and Hlasiwetz (p. 161) regard as a product of the decomposition of creosote] by dissolving commercial creosote in excess of strong potash-ley, separating the undissolved oil, and boiling the alkaline solution for a long time after dilution with water (see xi, 149). The capnomor, which passes over with the watery vapour, is freed from creosote by agitation with strong potash-ley, then distilled with water, washed with dilute sulphuric acid, and after removal of the water, distilled by itself over chloride of calcium. Thus obtained, it begins to boil at  $180^{\circ}$ , the greater part distilling between  $200^{\circ}$  and  $208^{\circ}$ ; but, owing to a slight alteration caused by distillation, it leaves a small, viscid, dark-coloured residue. The portions distilling between  $200^{\circ}$  and  $208^{\circ}$  have sp. gr. 0.995 at  $15.5^{\circ}$ , and a constant composition (on an average 81.22 p. c. C., 7.82 p. c. H., and 10.96 p. c. O.) corresponding to the formula  $C^{20}H^{14}O^8$ . The same capnomor seems to be formed by the distillation of creosote with lime (xi, 149). (Völckel, *Ann. Pharm.* 86, 99.)

4. *Picamar*. — Obtained from that portion of the heavy tar-oil which on fractional distillation passes over with sp. gr. between 0.9 and 1.15. (*Berzelius, Jahresh.* 13, 354. Subsequently Reichenbach employs only tar-oil of sp. gr. 1.08—1.16.) The tar-oil is mixed with 8 pts. potash-ley of sp. gr. 1.16, allowed to stand for a few days in the cold, whereby picamar-potash gradually crystallises out (often occupying more than one-half the bulk of the liquid); the crystals are separated, purified by repeated crystallisation from boiling potash-ley, until the ley runs off

colourless, and decomposed by dilute phosphoric (or hydrochloric) acid; and the separated oil is rectified two or three times over dilute phosphoric acid, and lastly alone *in vacuo*. — Nearly colourless, transparent, thick oil; refracts light strongly; unctuous to the touch. Does not solidify at 20°; boiling point 285° with 715 mm. pressure; sp. gr. 1.10 at 20°. It has a faint and not unpleasant smell; its taste is unbearably bitter and burning, but the after-taste cooling like peppermint. Neutral. Becomes brown by boiling in the air; not inflammable by itself, but burns in a wick, or when heated, with a bright, smoky flame. Chlorine converts it into mould, and an oil insoluble in potash-ley; with bromine it gets hot and is coloured red-brown. Nitric acid changes it into a red-brown, greasy mass, without forming oxalic acid; oil of vitriol does not attack it below 150°. — Slightly soluble in water. With caustic potash (and likewise with ammonia, soda, baryta, and lime) it gives a crystallisable compound, which is decomposed by water or alcohol, but not by carbonic acid. Dissolves in oil of vitriol without decomposition below 150°; easily soluble in acetic acid; soluble in all proportions in wood-spirit, alcohol, ether, acetic ether, creosote, and sulphide of carbon. It dissolves sugar of lead, cupric acetate, camphor, oil of turpentine, resin, picric, and benzoic acids. (Reichenbach, *Berzel. Jahresb.* 13, 354; *Schw.* 67, 274; 68, 295, and 351.) Völckel (*Ann. Pharm.* 86, 103), could not succeed in obtaining Reichenbach's picamar.

5. *Pittacal* is produced by addition of baryta-water to impure alcoholic picamar, or to heavy tar-oil, the acids of which are not quite neutralized by caustic potash. It gives to the liquid a beautiful indigo-blue colour, which changes after some time into red or black. No method for preparing it in the pure state is given. Thrown down from its solutions as a flocculent precipitate, or obtained by evaporation, pittacal forms a dark-blue, brittle, staining mass, having the appearance of indigo, and a coppery or golden metallic lustre. It has no taste or smell, and is fixed and neutral. Unalterable by light and air. Becomes brown like mould at a high temperature and chars, giving off an ammoniacal smell. Nitric acid decomposes it. — It is not properly speaking soluble in water, but is so finely divided when shaken up with water that the mixture passes clear through a filter. It dissolves with crimson colour in diluted sulphuric or hydrochloric acid, and abundantly with aurora-red colour in acetic acid; alkalis restore the original blue colour: the smallest trace of ammonia suffices to do so in the acetic acid-solution. It is quite insoluble in free aqueous alkalis, and is precipitated by them from its aqueous or acid solution in blue flakes, which appear, under the microscope, to be made up of fine needles. It forms a black-blue combination with lime, and beautiful dark-blue precipitates, which are unaffected by caustic ammonia in excess, with (even slightly acid) solutions of sugar of lead, salt of tin, sulphate of cuprammonium, acetate of alumina, &c. By means of salt of tin and acetate of alumina, it can be made to dye cotton, wool, and linen. It is insoluble in alcohol, ether, and eupion. (Reichenbach, *Schw.* 68, 1.) Völckel (*Ann. Pharm.* 86, 103) did not succeed in obtaining Reichenbach's pittacal.

6. *Brunolic acid*. — Produced, at the same time as rosolic acid (xi, 153), by treatment of coal-tar with alkalis. Preparation xi, 153, 154. A vitreous, shining, easily pulverisable mass resembling



asphalt. Most of its compounds are brown and insoluble. It dissolves in *alcohol*. (Runge, *Pogg.* 31, 71.)

### *Second Appendix to Cellulose.*

## 1. Ligno-sulphuric Acid.

BRACONNOT. *Ann. Chim. Phys.* 12, 185; *Schw.* 27, 340; *Gill.* 63, 360.

BLONDEAU DE CAROLLES. *Rev. scient.* 14, 476; *J. pr. Chem.* 32, 459.

MARCHAND. *J. pr. Chem.* 35, 200.

*Holzschwefelsäure, Pflanzenschwefelsäure; Acide végétal-sulfurique ou sulfolignique.*

The copulated acid formed by the action of oil of vitriol on cellulose is identical, according to Gerhardt (*Traité*, 2, 548), with sulphamidonic acid. If, however, as Béchamp's investigations render probable, cellulose-dextrin is different from starch-dextrin, it will follow that there must be a difference between the two acids, even though existing experiments do not suffice to prove it. (Kr.)

*Formation.* By the action of oil of vitriol on hemp, linen, cotton, or paper; the gum (Béchamp's cellulose-dextrin) which is first formed, uniting with the sulphuric acid. (Braconnot.)

*Preparation.* The solution obtained by triturating cotton-wool with oil of vitriol is mixed, as soon as it is clear, with a large quantity of water, and the solution is neutralised with carbonate of lead or carbonate of baryta; from the resulting solution of ligno-sulphate of lead or of baryta hydrosulphuric or carbonic acid separates ligno-sulphuric acid; the solution is evaporated to dryness, the residue dissolved in water and precipitated with *ether-alcohol*. (Blondeau.)—Marchand allows oil of vitriol to stand for four weeks upon Swedish paper, neutralises the diluted solution with lime, and separates the acid from the lime-salt.

*Properties.* Uncrystallisable, strongly acid syrup.

Becomes brown at a gentle *heat*, and blackens below  $100^{\circ}$ , yielding sulphuric acid and charcoal; it blackens more quickly above  $100^{\circ}$ , and evolves sulphurous acid. (Braconnot.)—The aqueous acid splits up into sulphuric acid and dextrin when heated. (Blondeau.)

*Combinations.* Deliquesces in the air and dissolves easily in *water*.

*With Bases.*—*Ligno-sulphates.*—The aqueous acid dissolves metallic oxides and carbonates and forms amorphous deliquescent salts. (Braconnot.) These salts evolve sulphurous acid when heated and leave a residue of sulphate and charcoal. (Braconnot.)—The baryta-salt and lead-salt are decomposed by carbonic acid. (Blondeau.)

*Ligno-sulphate of Baryta.*—The aqueous solution of this salt obtained in the preparation of ligno-sulphuric acid is evaporated *in vacuo*. (Blondeau.)

Calculation according to Blondeau de Carolles.

Blond. de Carolles.

18 C.....	108	....	24.79	....	24.46
19 H .....	19	....	4.36	....	4.25
19 O .....	152	....	34.92	....	36.19
2 SO <sup>3</sup> .....	80	....	18.37	....	18.00
BaO.....	76.5	....	17.56	....	17.10
<hr/>					
C <sup>18</sup> H <sup>18</sup> O <sup>18</sup> , 2SO <sup>3</sup> , BaO, HO .....	435.5	....	100.00	....	100.00

*Ligno-sulphate of Lime.*—*a.* By saturating the aqueous acid, obtained as above described, with chalk and evaporating the filtrate, a colourless gum is obtained, which is easily decomposed by heat, is deliquescent and readily soluble in water.—*b.* The solution obtained by the action of oil of vitriol on cellulose for 12 hours is diluted and saturated with chalk; the solution evaporated *in vacuo*, gives a pale yellow mass, which is decomposed by heat in the same way as the lead-salt.—*c.* Oil of vitriol is allowed to act on cellulose for 24 hours, and the product treated as in *b.* (Blondeau.)

	Blondeau de Carolles.			Marchand.	
	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	
C .....	27.43	....	21.62	....	46.42
H .....	5.16	....	4.42	....	6.68
O .....	40.82	....	34.49	....	15.34
SO <sup>3</sup> .....	19.70	....	28.90	....	43.62
CaO .....	6.89	....	10.57	....	15.36
<hr/>					
	100.00	....	100.00	....	100.00

*d.* Prepared from paper.—Blondeau de Carolles gives the following formulæ: for *a*, C<sup>18</sup>H<sup>18</sup>O<sup>18</sup>, 2SO<sup>3</sup>, CaO, 2HO; for *b*, C<sup>10</sup>H<sup>10</sup>O<sup>10</sup>, 2SO<sup>3</sup>, CaO, 2HO; for *c*, C<sup>4</sup>H<sup>4</sup>O<sup>4</sup>, 2SO<sup>3</sup>, CaO, 2HO. According to Marchand, *d* = C<sup>33</sup>H<sup>24</sup>O<sup>8</sup>, 2CaO, SO<sup>3</sup>.

*Ligno-sulphate of Lead.*—Obtained by evaporating *in vacuo* the solution obtained in the preparation of ligno-sulphuric acid.—Feathery crystals, or, when thoroughly dried *in vacuo*, a white pulverulent mass.—Softens at 100°, becomes darker coloured and then golden yellow. At a little above 100° it evolves carbonic oxide and sulphacetic acid, the strongly smelling vapour of which excites tears. When long boiled with water, it yields a precipitate of sulphate of lead while grape-sugar (whose composition corresponds to the formula C<sup>18</sup>H<sup>18</sup>O<sup>18</sup>) and sulphuric acid remains in solution.—Deliquesces in the air to a thick syrup, and dissolves readily in water.—*Chlorine*, in aqueous ligno-sulphate of lead, produces hydrochloric acid, oxide of lead, and a peculiar gum, but no sulphate of lead.—Insoluble in alcohol and ether. (Blondeau de Carolles.)

Calculation according to Blondeau de Carolles.

Blondeau de Carolles.

18 C .....	108	....	22.51	....	21.07
20 H .....	20	....	4.17	....	4.21
20 O .....	160	....	32.67	....	32.98
2 SO <sup>3</sup> .....	80	....	16.88	....	18.63
PbO .....	111.7	....	23.77	....	23.11
<hr/>					
C <sup>18</sup> H <sup>18</sup> O <sup>18</sup> , 2SO <sup>3</sup> , PbO, 2HO .....	479.7	....	100.00	....	100.00

## 2. Ternitrocellulose.



BÉCHAMP. *N. Ann. Chim. Phys.* 46, 342; abstr. *Compt. rend.* 41, 817; *J. pr. Chem.* 68, 51.

*Cellulose trinitrique.* (Béchamp.)

*Formation.* 1. By the action of alcoholic potash on pyroxylin dissolved in ether-alcohol, whereby two-thirds of the nitrogen separate as nitrate of potash. (Béchamp. — *Comp.* p. 178) — 2. In the preparation of gun-cotton with nitric acid of sp. gr. 1.41 — 1.45, the chief product is ternitrocellulose; quintonitrocellulose is also formed when fuming nitric is used. (Gladstone, *Mem. Chem. Soc.* 3, 412.)

*Properties.* When freshly precipitated, resembles gelatinous silica; shrinks to an amorphous yellowish gum by drying at the common temperature or at 100°. Hard and pulverisable. (Béchamp.)

				Gladstone.	Béchamp. mean, at 100°.	
24 C	144	...	31.37	...	30.85	31.01
3 N	42	...	9.15	...	—	9.60
17 H	17	...	3.72	...	3.76	4.27
32 O	256	...	55.76	...	—	55.12
$C^{24}X^3H^{17}O^{20}$	459	...	100.00	...	...	100.00

According to Béchamp, it contains nitric acid as a proximate constituent. See p. 174

*Decompositions.* 1. Ternitrocellulose (prepared by process 2) kept for some years exposed to *light*, evolved nitric acid vapours and was changed into gum. (Gladstone.) — 2. Not altered at 160°, but *explodes* at 168°, leaving a large residue of charcoal. (Béchamp.) — 3. *Nitro-sulphuric acid* converts the product of process 2 into gun-cotton. (Gladstone.) — 4. Dissolved by boiling *hydrochloric acid* with evolution of chlorine. (Béchamp.) — 5. *Sulphuretted hydrogen* decomposes the alcoholic solution, precipitating sulphur and afterwards flakes containing sulphur, which dissolve in water, are precipitated therefrom by alcohol, and do not explode by heat. — 6. Aqueous *ferrous chloride* converts it into amorphous cellulose. (Béchamp.)

*Combinations.* Insoluble in *water*; dissolves readily in fuming *nitric acid*. (Béchamp.) As obtained by process 2, it is soluble in nitric acid of sp. gr. 1.25 — 1.5, and in *oil of vitriol*. (Gladstone.) Dissolves easily in fuming *hydrochloric acid*, and is precipitated therefrom by water; also in dilute *potash-ley*, whence it is precipitated by acids; and in boiling, but not in cold, *glacial acetic acid*. (Béchamp.)

*Ammoniacal sugar of lead* throws down a white precipitate from an alcoholic solution to which enough water has been added to produce incipient turbidity. (Béchamp.)

Forms with *alcohol* a very fluid, easily filtered solution, from which water throws down a finely divided precipitate which balls together on drying or on addition of ether. (Béchamp.)

Soluble in *ether*. (Béchamp.) Fibrous ternitrocellulose dissolves with difficulty in *alcohol*, *ether*, *ether-alcohol*, and *acetic ether*; powdery ternitrocellulose dissolves easily in these liquids, also in *glacial acetic acid*. (Gladstone.)

### 3. Quadrinitrocellulose.



BÉCHAMP. *N. Ann. Chim. Phys.* 37, 207; *J. pr. Chem.* 68, 15. — *N. Ann. Chim. Phys.* 46, 347.

*Cellulose tétranitrique.*

*Formation and Preparation.* The thick solution of pyroxylin in 40 pts. ether and 15 pts. alcohol of 86 p. c. becomes quite fluid when ammonia gas is passed into it for half an hour, and, when then poured into a large quantity of water, yields quadrinitrocellulose in the form of a white powder.

*Properties.* A light, white powder, without taste or smell; becomes electric by friction. When dried over oil of vitriol at 20°, it retains 1.73 p. c. water, which goes off slowly at 100° (1 at. HO = 1.72 p. c.)

	at 100°.		Béchamp. mean.	
24 C .....	144	....	28.07	.... 28.22
4 N .....	56	....	10.92	.... 10.78
17 H .....	17	....	3.31	.... 3.57
37 O .....	296	....	57.70	.... 57.43
<hr/>				
$\text{C}^{24}\text{X}^4\text{H}^{17}\text{O}^{21}$ .....	513	....	100.00	.... 100.00

Béchamp gives the rational formula  $\text{C}^{24}\text{H}^{17}\text{O}^{17}, 4\text{NO}^5$  (see p. 174); the formula  $\text{C}^{24}\text{X}^4\text{H}^{16}\text{O}^{20}$ , which contains 1 at. HO less, is also admissible according to his analyses.

*Decompositions.* Evolves red vapours when heated in a tube to 145°–150°; explodes at 158°, leaving a residue of charcoal. — Evolves chlorine in abundance when heated with fuming *hydrochloric acid*. — Remains apparently unchanged by *nitro-sulphuric acid*; dissolves in fuming *nitric acid*, and is precipitated therefrom (perhaps as quinquenitrocellulose) by water. — Slowly converted by *sulphuretted hydrogen* in an ether-alcoholic solution, into the same products as ternitrocellulose. — Converted by *ferrous chloride* into amorphous cellulose. — Insoluble in dilute *potash-ley*; dissolves with decomposition in strong ley: acids precipitate ternitrocellulose from the solution.

Insoluble in *water*; dissolves slowly, without evolution of gas, in *oil of vitriol*. Insoluble in *glacial acetic acid* either cold or warm. Does not dissolve in either *alcohol* or *ether*, but dissolves very easily in *ether-alcohol*; water throws down from the solution flocks which do not ball together.

## 4. Pyroxylin.

- OTTO (1846). *Augsb. Allg. Zeitung*, vom 5 Octbr. 1856; *J. pr. Chem.* 40, 193; abstr. *Compt. rend.* 23, 807.
- SCHÖNBEIN & BÖTTGER. *Allg. Zeitung*. 1847, Nro. 3, Beilage, 21; *Pogg.* 70, 320; *Compt. rend.* 23, 678.
- DUMAS. *Compt. rend.* 23, 806 and 983.
- SCHÖNBEIN. *Bibl. univers.* [4] 3, 18; *Ann. des Scienc. phys. natur.* 4, 20 and 28.
- PELOUZE. *Compt. rend.* 23, 809, 838, 861, 892 and 1020.— *Compt. rend.* 24, 2; *J. pr. Chem.* 40, 414.
- KNOP. *Compt. rend.* 23, 808.
- AVÉROS. *Compt. rend.* 23, 874; *J. pr. Chem.* 40, 197.
- FORDOS & GÉLIS. *Compt. rend.* 23, 982.
- GAUDIN. *Compt. rend.* 23, 980 and 1099; abstr. *J. pr. Chem.* 40, 418.
- PAYEN. *Compt. rend.* 23, 999 and 1096.— *Compt. rend.* 24, 81.
- COTTEREAU. *Compt. rend.* 23, 1157; abstr. *J. pr. Chem.* 40, 418.
- MÉNARD & FLORES DOMONTE. *Recueil des trav. de la Soc. Pharm.* 1847, 104; abstr. *N. J. Pharm.* 12, 159.— *Compt. rend.* 23, 1087.— *Compt. rend.* 24, 87; abstr. *J. pr. Chem.* 40, 421.— *Compt. rend.* 24, 390.
- VAN KERCKHOFF. *Compt. rend.* 23, 1140; *J. pr. Chem.* 40, 284.
- VAN KERCKHOFF & REUTER. *J. pr. Chem.* 40, 262.
- SCHMIDT & HECKER. *J. pr. Chem.* 257.
- PELIGOT. *Compt. rend.* 23, 1085.
- DE VRIJ. *Compt. rend.* 24, 19; abstr. *J. pr. Chem.* 40, 420.
- SOBRERO. *Compt. rend.* 24, 247; abstr. *J. pr. Chem.* 40, 421.
- RANSOME. *Phil. Mag. J.* 30, 1.
- PORRETT & TESCHEMACHER. *Phil. Mag. J.* 30, 273; *Mem. Chem. Soc.* 3, 258.
- PORRETT. *Phil. Mag. J.* 30, 409; *Mem. Chem. Soc.* 3, 287; *J. pr. Chem.* 41, 208.
- WALTER CRUM. *Phil. Mag. J.* 30, 426; *J. pr. Chem.* 41, 201; *Ann. Pharm.* 62, 233.
- GLADSTONE. *Mem. Chem. Soc.* 3, 412; *Pharm. J. Trans.* 11, 401.
- JEAN. *Compt. rend.* 24, 1053.
- SOUBEIRAN. *N. J. Pharm.* 14, 263.
- BÉCHAMP. *N. Ann. Chim. Phys.* 37, 207; abstr. *Compt. rend.* 35, 473; *Inst.* 1852, 318; *N. J. Pharm.* 22, 440; *J. pr. Chem.* 58, 15; *Pharm. Centr.* 1852, 823.— *Compt. rend.* 37, 134; *Inst.* 1853, 261; *J. pr. Chem.* 60, 187; *Pharm. Centr.* 1853, 703.— *N. Ann. Chim. Phys.* 46, 338; abstr. *Compt. rend.* 41, 817; *J. pr. Chem.* 68, 51.
- MANN. *J. pr. Chem.* 59, 241.
- HADOW. *Chem. Soc. Qu. J.* 7, 201; *Chem. Centr.* 1855, 202; *J. pr. Chem.* 64, 169.

*Gun-cotton.* — *Schiessbaumwolle*, *Explodirende Baumwolle*. — *Pyroxyly* (Pelouze), *Fulmin* (Marx), *Coton azotique* (Gaudin), *hypoazotique* (Payen), *Coton fulminant*, *Tissu diélectrique explosif* (Meynier), *Cellulose nitrée* or *pentanitrique* (Béchamp), *Poudre-coton*, *Coton-poudre*, *Fulmicoton*.

The explosive substances prepared by Pelouze in 1838 (*Compt. rend.* 7, 713;

*J. pr. Chem.* 16, 168), by treating cotton-wool, paper, and hemp with nitric acid, were regarded as identical with xyloïdin, until Schönbein in 1846 announced the discovery of explosive cotton-wool applicable as a substitute for gunpowder. The method of preparing it, which he kept secret, or at any rate a method which equally yielded pyroxylin, was immediately afterwards discovered by Böttger and by Otto, and published by the latter. Knop afterwards advantageously substituted nitro-sulphuric acid for the concentrated nitric acid employed by Otto in the preparation of pyroxylin.

Pyroxylin prepared according to the methods given below seldom consists of a *single* substance, but is, for the most part, a mixture of several compounds, apparently of ter-, quadri-, and quintonitrocellulose, the latter of which chiefly prevails, and is perhaps under certain conditions obtained by itself. (For details see below.)

*Formation.* 1. By treating cotton-wool with fuming nitric acid. (Otto.) Ter- and quinto-nitrocellulose are thus formed. (Gladstone.)—2. By treatment with nitro-sulphuric acid. (Knop.)—3. By treatment with a freshly prepared mixture of saltpetre and oil of vitriol. (Millon & Gaudin.) Pyroxylin prepared according to 2 and 3 consists essentially of quinto-nitrocellulose. (Gladstone, Béchamp.)—Paper (Pelouze), wood, and sawdust are similarly converted into explosive compounds by treatment with the above mixtures. (Bley, *Compt. rend.* 23, 809; comp. also Bonjean, *Compt. rend.* 24, 190); also the epidermis of the cactus. (Payen.)

In the transformation of cotton into pyroxylin, water is the only other product formed. (Pelouze and others.)

An explosive substance whose identity with pyroxylin seems doubtful (see p. 86 and p. 106) is likewise formed by dissolving starch in nitrosulphuric acid (De Vrij, *Compt. rend.* 24, 19), or by dissolving xyloïdin in nitric acid and precipitating with sulphuric acid. (Cottureau, *Compt. rend.* 24, 205.)

*Preparation.* Purified cotton-wool is immersed in an appropriate mixture of saltpetre and oil of vitriol, or of nitric acid and oil of vitriol, allowed to remain in it a shorter or a longer time according to the degree of concentration and the temperature of the mixture, then washed, first with rain-water, afterwards with distilled water, till the adhering acid is completely removed, and finally dried. For the preparation of collodion, or pyroxylin soluble in ether-alcohol, the acid mixtures employed are different from those used for the preparation of explosive pyroxylin, as will be seen from what follows.

*a.* To obtain explosive pyroxylin. Purified cotton-wool is immersed in a mixture, previously cooled to 10° or 15°, of 1 measure nitric acid of sp. gr. 1.45—1.50 with 3 measures oil of vitriol of sp. gr. 1.85, and the imbibition of the acid is rendered as uniform as possible by stirring and dividing the wool. The greater part of the acid is removed from the cotton-wool by pressing it with a pestle; it is then allowed to stand for an hour; washed in a stream of water till all acid reaction has disappeared, and finally with a very dilute solution of potash, and dried at 65°. (Schönbein, *Dingl.* 104, 450; *Lieb. Kopp. Jahresber.* 1847-1848, 1142.)

*b.* To obtain pyroxylin soluble in ether-alcohol (collodion-wool). 1 ounce of cotton-wool is plunged into a mixture (which should be prepared

immediately before use) of 16 oz. saltpetre, 12 oz. common oil of vitriol, and 12 oz. Nordhausen sulphuric acid; it is stirred without interruption for 5 minutes; the whole contents of the vessel are then poured into a large quantity of hot water; and the cotton is collected, and washed in a tin colander till all adhering acid is thoroughly removed. (*N. Br. Arch.* 104, 274.) If the operation is performed with the foregoing quantities, and the saltpetre thrown cold into the acid, the mixture possesses, immediately after being made, a temperature of  $68^{\circ}$ — $71^{\circ}$ , which is the temperature which answers best for the preparation of collodion-wool.

1. *Preliminary treatment of the cotton-wool.* The cotton is boiled for some hours with weak soda-ley, and then well washed with water, next with very dilute hydrochloric acid, and lastly again with water. (van Kerchoff & Reuter.) Carded cotton is treated successively, at the boiling heat, with weak soda-ley, solution of chloride of lime, dilute nitric acid, and water. (Walter Crum.)—Schmidt & Hecker chop up the cotton-wool till it becomes like cloth-shearers' dust. Bérard\* (*Polyt. Centr.* 1858, 892) employs cotton-shearings (*Scherflocken der Baumwolle*) of which the same quantity of acid can moisten a larger quantity than of carded cotton.

2. *Processes with nitric acid alone.* Cleaned cotton-wool dipped for half a minute into fuming nitric acid, then immediately into frequently renewed water, so as perfectly to remove all adhering acid, and dried, is changed into an explosive substance, which explodes under the hammer like fulminating mercury, and burns away like gunpowder when touched with a spark. (Otto, *J. pr. Chem.* 40, 193.)—100 pts. cotton-wool left in contact with nitric acid, whether for a few minutes or for several days, yield 168—170 pts. pyroxylin. (Pelouze, *Compt. rend.* 23, 892; *J. pr. Chem.* 40, 200.)

By dissolving cotton-wool in nitric acid of sp. gr. 1.45 and precipitating the solution with water, ternitrocellulose is obtained. (Gladstone, *Chem. Soc. Mem.* 3, 412.)

3. *Processes with nitro-sulphuric acid.* 1 pt. (or more: Knop) fuming nitric acid is mixed with 1 pt. oil of vitriol and allowed to stand (at least 3 minutes: van Kerckhoff & Reuter) a few minutes or longer (Knop). For 1 measure oil of vitriol, Pelouze takes 1 measure fuming nitric acid; Walter Crum takes 3 measures; Ransome, 2 measures; Meynier (*Compt. rend.* 26, 44)  $\frac{3}{2}$  measure. Gaudin immerses the cotton-wool for a few seconds; Meynier and Walter Crum for an hour.—De Vrij mixes the cotton-wool rapidly with nitric acid, warms the mixture to  $30^{\circ}$  or  $35^{\circ}$ , and precipitates the solution (which is at first thick and turbid, but afterwards becomes clear) with oil of vitriol.

Edwards (*J. Chim. méd.* 25, 54) prepares collodion-wool with equal measures of oil of vitriol and of nitric acid of sp. gr. 1.52, allowing the mixture to act for 1 minute; Hadow uses 104 pts. oil of vitriol of sp. gr. 1.833 and 89 pts. nitric acid of sp. gr. 1.424, and operates at  $55^{\circ}$ .

If the acids are either too concentrated or too dilute, they do not give soluble collodion-wool; the following are, however, good proportions:—13 pts. sulphuric acid of sp. gr. 1.632, 12 pts. nitric acid of sp. gr. 1.512–1.518, and 1 pt. cotton-wool; or, 45 pts. sulphuric acid of sp. gr. 1.75, 12 pts. nitric acid of sp. gr. 1.512–1.518, and 1 pt. cotton-wool. The mixture is cooled to  $5^{\circ}$ , the cotton-wool stirred in, and the

whole allowed to stand for 24 hours in a covered vessel at  $5^{\circ}$ – $8^{\circ}$ . At  $40^{\circ}$ – $50^{\circ}$ , one hour suffices for the action, the collodion-wool obtained is not however always equally good. Collodion-wool which has been rendered insoluble by using too strong sulphuric acid may be made soluble by treatment with the proper mixture of acids; and, inversely, soluble collodion-wool can be rendered insoluble by very concentrated acids. (Mann.)

Hadow added to a mixture of 1 at. nitric acid ( $\text{NO}^5\text{HO}$ ), with 2 at. sulphuric acid ( $\text{SO}^3\text{HO}$ ), quantities of water increasing from 1 to 5 atoms, and obtained with the resulting liquids pyroxylin of variable properties. 100 pts. cotton-wool, dried at  $100^{\circ}$ , were converted, by several hours' action of the mixture  $\text{NO}^5\text{HO} + 2(\text{SO}^3\text{HO}) + \text{HO}$ , into 177 pts. pyroxylin (weighed after drying *in vacuo* over oil of vitriol), which was insoluble in ether-alcohol. 100 pts. cotton-wool acted on by the mixture  $\text{NO}^5\text{HO} + 2(\text{SO}^3\text{HO}) + 2\text{HO}$  became 176 pts. pyroxylin, and with the mixture  $\text{NO}^5\text{HO} + 2(\text{SO}^3\text{HO}) + 3\text{HO}$ , 171.7 pts. pyroxylin, like the first, nearly insoluble. Mixtures of nitric and sulphuric acid in the above proportions, but containing  $3\frac{1}{2}$ ,  $3\frac{2}{3}$ , 4, and 5 atoms water yielded respectively 166.4, 160.5, 157, and 140 pts. of a product soluble in ether-alcohol, but repetition of the experiments did not give exactly the same results. At  $15^{\circ}$ , the mixture  $\text{NO}^5\text{HO} + 2(\text{SO}^3\text{HO}) + 3\text{HO}$  gave a product soluble in ether-alcohol; at  $55^{\circ}$ , a product insoluble in ether-alcohol. Mixtures containing more water yielded soluble products at both temperatures; but the pyroxylin prepared at a low temperature formed thick, glutinous solutions; that prepared at a higher temperature perfectly fluid solutions. (Hadow.)

When the acid mixture is saturated with hyponitric acid, it attacks the cotton-wool more violently; but yields a slightly explosive product, which dissolves in ether-alcohol; whereas nitro-sulphuric acid, containing no hyponitric acid, yields a large quantity of highly explosive pyroxylin. (Pelouze, *Compt. rend.* 24, 86.)

c. *Processes with saltpetre and oil of vitriol.* All these processes aim at the production of collodion-wool. — Mialhe (*N. J. Pharm.* 24, 263) employs, for 1 pt. cotton-wool, 20 pts. dry saltpetre and 30 pts. fuming sulphuric acid, and allows the action to go on for 3 minutes. Livonius (*N. J. Pharm.* 16, 122) and Magnes-Lahens (*N. J. Pharm.* 16, 353) operate in the same way, but employ common oil of vitriol and allow the action to continue for 5 minutes.

Mann recommends as the best mixture 20 pts. saltpetre, and 31 pts. oil of vitriol of sp. gr. 1.83 to 1.835; he allows the mixture to cool to below  $50^{\circ}$ , and then lets 1 pt. cotton-wool lie in it for 24 hours at  $28^{\circ}$  or  $30^{\circ}$ . If the cotton-wool remains for 5 or 6 days in the mixture, at about  $30^{\circ}$ , the product is all the better; if the action is only continued for 16 or 20 minutes the product is imperfect. He also obtained good collodion-wool with the following mixtures: 1 pt. cotton-wool to 10 pts. saltpetre and 33 pts. sulphuric acid of sp. gr. 1.80; 1 pt. cotton-wool to 17 pts. nitrate of soda and 68 pts. sulphuric acid of sp. gr. 1.79, or to 34 pts. nitrate of soda and 66 pts. sulphuric acid of sp. gr. 1.80. When nitrate of soda is used, the acid mixture is allowed to stand 24 hours before the cotton-wool is put into it; the cotton-wool is then left in it for 5 days at  $30^{\circ}$ .

According to Legray (*Gerhardt, Traité*, 2, 509) excellent collodion for photographic purposes, and completely soluble in ether, is obtained



by operating as follows:—80 grammes powdered nitrate of potash is placed in a capacious dish, 120 grammes concentrated sulphuric acid is poured upon it, and the whole well mixed; 4 grammes cotton-wool is then added and stirred about in the mixture for 10 minutes, after which it is taken out and thoroughly washed with water; the product is injured by allowing it to remain in the acid for a longer time.

In order to obtain soluble collodion-wool with a mixture of 2 pts. saltpetre and 3 pts. oil of vitriol, the cotton-wool should be dipped into the mixture while it is still warm from the heat produced in the reaction, not after it has cooled. (Béchamp.) The following experiments confirm this statement, but according to the results obtained by Mann, it appears that, when less concentrated sulphuric acid is employed, long continuance of the action produces the same result as an increase of temperature. [Kr.] See also Hadow, p.

1 oz. cotton-wool, immersed in a mixture of 16 oz. dried saltpetre and 24 oz. Nordhausen sulphuric acid at  $81^{\circ}$ , yields 127 p. c. pyroxylin, insoluble in ether, and but slightly explosive.

With common sulphuric acid, instead of Nordhausen acid, 109 p. c. pyroxylin, of similar properties, is obtained by 10 minutes' action at  $56^{\circ}$ , 102 p. c. by  $\frac{1}{4}$  hour's action (or, with constant stirring, 108 p. c. explosive, partially soluble pyroxylin), and only 36 p. c. by 1 hour's action. On the other hand the mixture of 16 oz. saltpetre, 12 oz. Nordhausen acid, and 12 oz. common sulphuric acid, mentioned at p. 169, yields with 1 oz. cotton-wool, at  $68^{\circ}$ – $71^{\circ}$ , 123 p. c. soluble collodion-wool in 3 to 4 minutes, but only 102 p. c. in 20 to 25 minutes. Insoluble collodion can also be rendered soluble by treatment with this mixture.

¶. Pyroxylin soluble in alcohol may be obtained by immersing cotton-wool in a mixture of 4 pts. by weight of sulphuric acid of sp. gr. 1.84 and 3 pts. nitric acid of sp. gr. 1.40; decanting the acid after five minutes' immersion; pouring the pyroxylin into a bucket of water; agitating it, with frequent renewal of the water; leaving it immersed over night; repeating the washings in the morning; and then spreading it out on a table to dry. The washing must be performed with care, as the pyroxylin is of pulverulent texture, and is easily washed away. The strength of the acids used in the preparation is of especial importance; if they are too weak, the cotton dissolves; if too strong, the pyroxylin produced is insoluble in alcohol. (Sutton, *Rép. Chim. app.* 4, 145). ¶.

100 pts. cotton-wool yield 154 pts. pyroxylin (Teschemacher & Porrett); 169 pts. (Teschemacher); 177.9 pts. (Walter Crum); 150–170 pts. (Fehling); 168–170 pts. (Pelouze); 100 pts. Swedish paper yield 175 pts. pyroxylin (Pelouze); 169 pts. (Hecker & Schmidt); 176.2 pts. (van Kerckhoff & Reuter); 173–175.2 pts. according to Schönbein's process (Gladstone, *Lieb. Kopp. Jahresber.* 1847–1848, 1137); 164.1 pts. (Ransome); 142–175 pts., varying according to the quantity and degree of concentration of the acids (Gladstone); 201.5 pts. (Soubriesscau.)

*Properties.* Pyroxylin prepared from cotton-wool retains the external properties of the wool, but is usually somewhat harsher to the touch. It has neither taste nor smell, and is neutral to moistened litmus-paper. — By friction it becomes more strongly electric than cat's skin; it crackles, yields sparks, and is phosphorescent in the dark. (Gaiffe, *Compt. rend.* 24, 88.) The fibres of pyroxylin seen under the micro-

scope, by polarised light, exhibit very little brightness, and scarcely any play of colours; whereas the fibres of common cotton-wool appear bright and show a beautiful play of colours in the dimmest light. (Kindt, *Pogg.* 70, 168.)

## Calculations.

a.				b.			
24 C	144	28.57		24 C	144	26.23	
16 H	16	3.17		15 H	15	2.73	
4 N	56	11.11		5 N	70	12.75	
36 O	288	57.15		40 O	320	58.29	

$C^{24}H^{16}X^4O^{20}$	504	100.00		$C^{24}H^{15}X^5O^{20}$	549	100.00	
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c.				d.			
24 C	144	21.24		24 C	144	25.39	
14 H	14	2.35		17 H	17	2.99	
6 N	84	14.14		5 N	70	12.34	
44 O	352	59.27		42 O	336	59.28	

$C^{24}H^{14}X^6O^{20}$	594	100.00		$C^{24}H^{17}O^{17}, 5NO^5$	567	100.00	
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	Schönbein & Böttger.	Domonte & Ménard.		van Kerckhoff & Reuter.	Hecker & Schmidt.
		a.	b.		
C	27.43	28.5	23.38	24.59 to 25.03	24.73 to 26.06
H	3.54	3.5	2.92	2.49 — 2.59	2.68 — 2.94
N	14.26	11.6	11.36	13.81 — 14.83	12.26 — 13.50
O	54.77	56.4	62.34	58.14 — 58.70	59.22 — 59.77

100.00    100.0    100.00

	Ransome.	Walter Crum.	Pelouze.	Gladstone.
C	26.16	24.69	25.2 to 25.8	26.1 to 27.9
H	3.14	2.48	2.9 — 2.3	3.22 — 3.33
N	10.20	13.80	12.6 — 13.0	12.75
O	60.50	59.03	59.3 — 58.9	

100.00    100.00    100.0    100.0

	Roser & Krauss.	Porrett & Teschemacher.	Péligot.
C	25.9 to 26.7	26.77	22.17
H	3.7 — 4.1	2.22	2.80
N	9.3 — 11.0	17.84	
O		54.87	

Schönbein & Böttger investigated pyroxylin which had been dissolved in acetic ether; Domonte & Ménard pyroxylin insoluble (a) and (b) soluble in ether-alcohol; Roser & Krauss analysed air-dried pyroxylin; v. Kerckhoff & Reuter dried theirs in vacuo; Pelouze, his at 40°—55°; Schmidt & Hecker, theirs at 90°—100°.

The formulæ a, b, c, represent pyroxylin as cellulose which has taken up 3, 4, or 5 at. nitric acid, with elimination of as many atoms of water. If for the purpose of comparing the different formulæ, we disregard for the moment whether the various authors have represented pyroxylin with  $C^{12}$  or with  $C^{24}$ , and as containing  $NO^4$  or  $NO^5$  as a proximate constituent, the various formulæ which have been proposed may be written thus:  $C^{24}H^{18}X^6O^{24}$  (Péligot.),  $C^{24}H^{16}X^5O^{21}$  (Schmidt & Hecker.),  $C^{24}H^{15}X^6O^{19}$  (van Kerckhoff & Reuter.),  $C^{24}H^{16}X^8O^{24}$  (Porrett & Teschemacher.),  $C^{24}H^{17}X^5O^{23}$  (Pelouze). The formula a was proposed by Gerhardt (*Traité*, 2, 504) for the product examined by Domonte & Ménard; the formula b was proposed by Gladstone; formula c, by Walter Crum. According to Gerhardt, the last formula represents the composition of the pro-

ducts examined by Gladstone, Pelouze, Schmidt and Hecker, and van Kerckhoff & Reuter. The formula  $d$ , first proposed by Pelouze, is also adopted by Béchamp; this chemist obtained from pyroxylin on an average 56.77 p.c. cotton-wool (calc. 57.14 p.c.) See also below.

Fehling gives the formula  $C^{24}H^{20}O^{20}, 4NO^5$ , according to which the formation of pyroxylin must be supposed to be accompanied by elimination of water from the nitric acid only, at least for the product examined by Roser & Krauss. The rapid dilution of the acids used for preparing pyroxylin is in opposition to this view. Schönbein & Böttger's formula,  $C^9H^6N^2O^{13}$ , is inadmissible, seeing that no second carbonised product is formed. Ransome's formula,  $C^{12}H^8O^{10}, 2NO^5$ , which involves the elimination of hydrogen, is equally inadmissible. Pettenkofer's formula,  $C^{12}H^7O^{18}, NO^5$ , is founded upon an incorrect nitrogen-determination. For Porrett's adventurous views see *Mem. Chem. Soc.* 3, 287; *Phil. Mag.* 30, 273; *J. pr. Chem.* 41, 208.

Domonte & Ménard assign the formula  $C^{24}H^{15}X^6O^{24}$  to that portion of pyroxylin which is soluble in ether, and the formula  $C^{24}H^{16}X^4O^{20}$  to the insoluble portion; the former in their *glucose sœnitrique*, the latter their *ligneux quadrinitrique*. Gaudin (*Compt. rend.* 23, 1099) distinguishes the soluble portion as *étherziline*.

According to Hadow, the action of nitrosulphuric acid on cotton-wool produces mainly three distinct products:

a.  $C^{12}H^7X^3O^{10}$ , or  $C^{24}H^{14}X^6O^{20}$ . Obtained, in the proportion of 181.34 pts. (calcul. 183.3 pts.) from 100 pts. cotton-wool, by repeated immersion in a mixture of 1 at. nitric acid ( $HIO, NO^5$ ), 2 at. oil of vitriol, and 3 at. water. Insoluble in ether-alcohol; soluble in acetic ether. Yields, when decomposed by sulphhydrate of potassium, 54.6 to 55.2 p. c. cotton-wool (calcul. 54.54 p. c.) and 44.07 p. c. hyponitric acid ( $NO^4$ ) after deducting the corresponding quantity of hydrogen (calcul. 45.46 p. c.).

b.  $C^{36}H^{22}X^6O^{30}$ . Obtained in the same way as a, when the acid mixture contains  $\frac{1}{2}$  at. more water, 100 pts. cotton-wool yielding 171.4 pts. of this compound (calcul. 174 pts.). Soluble in ether-alcohol; insoluble in acetic acid. Treated in the same manner as a, it yields 57.56 to 58.34 p. c. cotton-wool (calcul. 57.45 p. c.).

c.  $C^{56}H^{23}X^7O^{30}$ . The mixture employed for the preparation of a yields, when 1 at. water has been added to it (making 4 at. water in all), 164 p. c. of this substance (calcul. 164.8 p. c.). Soluble in ether and in glacial acetic acid. Gives by decomposition 60.66 p. c. cotton-wool (calcul. 60.67 p. c.). (Hadow.)

According to the views of most chemists, the nitrogen of pyroxylin is contained in the form of X (see vii. 73) replacing hydrogen; according to Béchamp (who has further extended the view previously propounded by Pelouze, Cottureau, and Walter Crum) it exists in the form of nitric acid ( $NO^5$ ). According to the former view, pyroxylin is comparable with nitrobenzoic acid, nitrobenzene, &c.; according to Béchamp's view, it is comparable with nitric ether (viii. 475). The following decompositions are favourable to the latter view: 1. Alkalis and reducing agents transform nitro-compounds into new substances containing nitrogen, but from pyroxylin they regenerate the original non-nitrogenous cotton-wool, just as they regenerate alcohol from nitric ether. (Béchamp.)—2. Pyroxylin behaves like a nitrate, not like a nitro-compound, with protosulphate of iron. (Cottureau, *Compt. rend.* 23, 1157.)—3. Pyroxylin, decomposed over mercury by oil of vitriol, behaves like a nitrate, giving off the whole of its nitrogen in the form of nitric oxide. (Walter Crum.)

*Decompositions.* 1. Under certain conditions which are not accurately known, and do not always occur, pyroxylin undergoes *spontaneous decomposition*, which is either accompanied by ignition and explosion, or takes place more slowly, unaccompanied by these phenomena.

On the 17th July, 1848, the explosion of 1,600 kilogrammes of gun-cotton, for which no cause could be ascertained, completely destroyed the manufactory at Bouchet. Walls, from  $\frac{1}{2}$  metre to 1 metre in thickness, were literally broken to powder from top to bottom, and the heaviest articles were hurled to great distances. (*Compt. rend.* 28, 345.) Similar explosions have taken place at Dartford, in Saxony, and at various other places. An explosion of pyroxylin took place in a magazine near Vincennes, which no one had entered for several days previously. (*Handwörterb.* 6, 723.)

Pyroxylin stowed away in casks in a dry place evolved a choking smell after  $3\frac{1}{2}$  to 9 months, contained formic acid, and as much as 11·5 p. c. water; probably because the sulphuric acid cannot be thoroughly removed by washing with water, and then causes decomposition to set in. — Pyroxylin, stored up in Glashaven, decomposed with evolution of gas, blowing out the stoppers of the bottles, and leaving as residue a soft white mass, which continued to evolve nitric oxide. (Maurey, *Compt. rend.* 28, 344.) — Pyroxylin, prepared in 1847, crumbled to powder with evolution of red fumes, after some time; after 12 years, the residue had deliquesced to a gum containing crystals of oxalic acid. (Hofmann, *Ann. Pharm.* 115, 283.) — A woven fabric, which had been converted into pyroxylin, evolved red vapours, after 3 years; after being then washed, it was less inflammable; and, when dried at 110°, contained 31·25 p. c. C., 4·08 p. c. H., and 7·88 p. c. N. (Kuhlmann & Wurtz, *Compt. rend.* 42, 676.)

2. Pyroxylin prepared with nitric acid explodes, like fulminating mercury, when *struck* upon an anvil with a hammer. (Otto.) Moderately strong strokes of a hammer upon pyroxylin cause it to fly to dust with a loud report but without flame. (Schönbein & Böttger.) Pyroxylin does not take fire when rubbed in a mortar with hard soda-glass. In other cases, pyroxylin takes fire by friction only when the heat produced is sufficient to make it do so. (Schönbein & Böttger.)

3. Pyroxylin is not decomposed, or only with difficulty, by the *electric current*. But if pyroxylin moistened with glacial acetic acid is placed between a silver and a zinc plate, connected by a copper wire, and allowed to remain for eight hours, a small quantity of substance is deposited on the silver plate, which, when dry, is white, has the appearance of starch, and blues litmus. (Porrett.)

4. By contact with a glowing match it takes fire and *burns* away instantaneously, like gunpowder. When *warmed* by itself, it either takes fire and explodes, or, when heated more slowly, is gradually decomposed with inflammation.

Pyroxylin may be exploded by touching it with a spark, when laid on the palm of the hand without causing pain, and when laid on a heap of gunpowder without setting fire to the latter. (Knop.) — Pyroxylin heated in an oil-bath does not take fire 130°; at 150°, it takes fire in 12 minutes; at 170°, in  $\frac{1}{2}$  minute; at 200°, in 12 seconds; at 230°, instantly, leaving no residue. (Schönbein & Böttger.) Payen observed the inflammation of pyroxylin, in a stream of heated

air, at  $25^{\circ}$ – $30^{\circ}$ ; Piobert, at  $70^{\circ}$ – $80^{\circ}$ . When heated in the air it takes fire at  $175^{\circ}$ – $180^{\circ}$  (Pelouze); at  $188^{\circ}$ . (Gladstone.) Pyroxylin prepared from carded cotton-wool does not take fire below  $200^{\circ}$ . (Payen.)

Pyroxylin placed at the bottom of a tube heated to  $200^{\circ}$ , whose temperature is gradually falling, still explodes at  $138^{\circ}$ , but not at lower temperatures. If the tube is quickly heated, so that the temperature rises  $12.5^{\circ}$  in a minute, the pyroxylin explodes sometimes at  $62.5^{\circ}$ ; generally in from 2 to 5 minutes at  $95^{\circ}$ . (Marx, *Pogg.* 78, 100.)

Pyroxylin when slowly heated gives off a smell of nitrous acid at  $100^{\circ}$ ; loses 10 p. c. of its weight in an hour between  $100^{\circ}$  and  $110^{\circ}$ ; becomes yellow and pulverizable, and then sometimes takes fire suddenly. (Pelouze.) Pyroxylin enclosed in glass tubes takes fire at  $132^{\circ}$  when quickly heated in an oil-bath; when slowly heated, not even at  $180^{\circ}$  or  $200^{\circ}$ . (van Kerckhoff.) If pyroxylin is heated slowly, so that the temperature rises  $6.25^{\circ}$  in a minute, it begins to evolve acid vapours at  $69^{\circ}$ , and then explodes with much less violence when lighted; at  $150^{\circ}$ , it scarcely explodes at all, and if kept for an hour at  $137^{\circ}$  it becomes yellowish brown, afterwards darker, and is at last converted into a black tissue which no longer explodes in the flame. (Marx.) Piobert and van Kerckhoff obtained similar results by slow heating.

The gases produced by the explosion of pyroxylin consist of nitrogen, carbonic acid, carbonic oxide, steam, nitrous acid or nitric oxide, hydrocarbons, ammonia, hydrocyanic acid or cyanogen; some of these gases are probably only formed under particular circumstances.

1 gramme pyroxylin, prepared with nitrosulphuric acid, yielded, on explosion in the vacuum of the barometer, 588 c. c. gas, measured at  $0^{\circ}$  and 760 mm. pressure. This gas contained, in 100 pts., 4.0 pts. nitrogen, 17.2 nitric oxide, 37.6 carbonic oxide, 20.8 carbonic acid, 4.6 carburetted hydrogen, and 15.8 steam. (Schmidt & Hecker.) Porrett & Teschemacher obtained, from 1 gramme pyroxylin, 483 c. c. gas, containing, in 100 pts., 7.14 pts. nitrogen, 35.72 nitric oxide, 35.72 carbonic oxide, 14.23 carbonic acid, and 7.14 cyanogen. Fordos & Gélis (*Compt. rend.* 23, 982) always found cyanogen or hydrocyanic acid, whether the explosion took place slowly or all at once, but ammonia only in small quantity. — The projectile force of pyroxylin exploded in fire-arms or in mines, is from  $1\frac{1}{2}$  to 6 times as great as that of gun-powder; the explosion takes place, however, too instantaneously, so that fire-arms are soon rendered useless, and frequently burst, by the employment of pyroxylin.

5. Pyroxylin moistened with moderately hot steam, and heated to  $100^{\circ}$ , evolves, sometimes more, sometimes less, nitric acid vapour, afterwards hyponitric acid vapour, and when coloured vapours are no longer given off, is found to have lost from 24.2 to 29.3 p. c. of its weight; it is thus converted into typhoxylin, or similar compounds, produced from pyroxylin by fixation of water and elimination of nitric (or hyponitric) acid. (van Kerckhoff & Reuter.) If the red fumes are too rapidly evolved, explosion may occur.

a.  $C^{14}N^2H^{16}O^{30}$ , van Kerckhoff & Reuter's *Typhoxylin*. — If the loss of weight by the pyroxylin amounts to 27 p. c., the residue, when dried in vacuo, contains on the average 33.49 p. c. C., 3.91 p. c. H., and

6.66 p. c. N. (calculation, 33.64 p. c. C., 3.73 p. c. H., 6.54 p. c. N.); it has therefore been formed by the fixation of 3 at. water, and elimination of 4 at. hyponitric acid:  $C^{24}N^6H^{13}O^{48} + 3H_2O = C^{24}N^2H^{16}O^{50} + 4NO^4$ . This typhoxylin has the appearance of pyroxylin, it is very easily powdered, pure white, becomes brown at  $150^\circ$ , more rapidly at  $170^\circ$ , and explodes when quickly heated, evolving nitric oxide and combustible gases. It is insoluble in cold nitric acid, dissolves slowly in warm nitric acid, easily in cold sulphuric acid and evolves gas when warmed therewith. Cold potash-ley dissolves it with yellow-brown colour, sugar of lead causes a precipitate in this solution. Ammonia and baryta-water colour typhoxylin light brown. It is only imperfectly soluble in ether or in acetic ether.

b.  $C^{24}N^2H^{17}O^{51}$ . When the loss of weight amounts to 24.2 — 24.9 p. c. (calcul. 25.3 p. c.), the residue contains, on an average, 32.87 p. c. C., 3.92 p. c. H. (calculation, 32.95 p. c. C., 3.88 p. c. H.), it is accordingly produced by fixation of 4 at. water and elimination of 4 at. hyponitric acid.

c.  $C^{24}N^2H^{17}O^{52}$ , and d.  $C^{24}N^2H^{18}O^{53}$ . The former compound is contained in the residue when the loss of weight amounts to about 30 p. c. (calc. 30.8 p. c.), and contains 35.78 p. c. C., and 4.68 p. c. H. (calculation, 35.55 p. c. C., and 4.20 p. c. H.). The latter compound contains, on an average, 34.61 p. c. C., and 4.30 p. c. H. (calculation, 34.78 p. c. C., and 4.34 p. c. H.) They are formed from pyroxylin by fixation, the former of 4 at., the latter of 5 at. water, and elimination of 4 at. nitric acid. (van Kerckhoff & Reuter.)

6. Pyroxylin moistened with *biniodide of potassium* (solution of iodine in aqueous iodide of potassium), and afterwards with a mixture of 1 pt. oil of vitriol and 4 pts. water, becomes yellow after some time, whereas unaltered cotton-wool is coloured blue. (Kindt, *Pogg.* 70, 168.)

7. Pyroxylin dissolves in concentrated *nitric acid* at  $80^\circ$  or  $90^\circ$ , and is precipitated almost completely by oil of vitriol in white amorphous flocks, otherwise unchanged; water precipitates it in bitter, white flocks, soluble in alcohol and in a large quantity of water, which burn more slowly than pyroxylin and leave charcoal. (De Vrij, *Compt. rend.* 24, 19.)

Pyroxylin is dissolved between  $38^\circ$  and  $67^\circ$  when warmed with 20 pts. nitric acid of sp. gr. 1.45: water added to the solution precipitates it unchanged, except that it has lost its organised structure. The nitric acid solution evolves abundance of red fumes if heated to  $113^\circ$ , and, when afterwards neutralised with carbonate and bicarbonate of potash, yields a whitish grey precipitate. (Porrett.)

8. It dissolves less readily than cotton-wool in cold *oil of vitriol*, more easily in sulphuric acid of sp. gr. 1.5 — 1.7. The solution evolves carbonic acid and nitrous gas at  $100^\circ$ , and does not become brown till more strongly heated (van Kerckhoff & Reuter), not even when boiled. (Gladstone.) The solution of cotton-wool in oil of vitriol becomes brown at  $90^\circ$  without evolving gas.

Bihydrated sulphuric acid neither dissolves pyroxylin nor becomes heated in contact with it, but soon evolves a smell of nitric acid. If water is added after 24 hours, the mixture filtered, and the filtrate

distilled, nitric acid passes over, and, when the residue in the retort gets more concentrated, red fumes are given off. (Béchamp, *N. Ann. Chem. Phys.* 46, 358).

9. Hot *hydrochloric acid* dissolves it with decomposition. (Béchamp.)

10. Moist *sulphurous acid* does not decompose it even on heating. (Béchamp.)—11. Not altered by *sulphuretted hydrogen* passed into its solution in ether-alcohol. (Béchamp.)

12. Pyroxylin moistened with water, or dissolved in ether-alcohol, is decomposed by gaseous *ammonia* into nitrate of ammonia and quadrinitrocellulose. (Béchamp.) The action of an excess of ammonia aided by heat, on pyroxylin moistened with water, yields a brown mass devoid of structure. (Béchamp.)

13. Pyroxylin is decomposed when heated with aqueous *hydrosulphate of ammonia*, and when washed and dried, no longer explodes by heat. (Pettenkofer, Marx.) If ammonia is passed into a solution of pyroxylin in ether-alcohol until it becomes perfectly fluid, and then sulphuretted hydrogen, a yellow precipitate containing sulphur is produced, which is insoluble in alcohol of 90 p. c., but partially soluble in water. (Béchamp.)

14. Moderately concentrated *potash-* or *soda-ley* dissolves pyroxylin slowly at the common temperature, more quickly between  $60^{\circ}$  and  $80^{\circ}$ , with formation of nitrates.

a. If the solution is filtered before all the pyroxylin is dissolved, and precipitated with dilute acid, a gelatinous precipitate is produced, probably containing quadri- or ter-nitrocellulose, which burns when dry, but leaves a large quantity of charcoal and is soluble in boiling alcohol, or in cold ether-alcohol. The solution may be diluted with a considerable quantity of water without becoming turbid; with ammoniacal acetate of lead, it produces a bulky precipitate. (Béchamp.)

b. The alkaline solution of pyroxylin becomes brown at  $50^{\circ}$  or  $60^{\circ}$ , and is then no longer precipitated by acids. If the solution is neutralised, shortly before this point, with dilute sulphuric acid, it leaves on evaporation a mixture of nitrate, nitrite, and sulphate of potash, with sugar, which last is converted, by further action of alkali, into glucic and apoglucic acids. (Béchamp.)

c. If the solution of pyroxylin in ether-alcohol is mixed with as much alcoholic potash as is required to neutralise the nitric acid, it solidifies to a jelly, and addition of water causes a pitch-like substance to separate, while scarcely any organic matter remains dissolved in the supernatant ether-alcohol. The pitch-like mass containing potash, when dissolved in water, yields a gelatinous precipitate of ternitrocellulose on addition of acetic acid.  $C^{24}H^{17}O^{17}, 5NO^5 + 2KO, HO = C^{24}H^{17}O^{17}, 3NO^5 + 2KO, NO^5 + 2HO$ . (Béchamp.)

According to van Kerckhoff (*J. pr. Chem.* 40, 284) an excess of moderately concentrated solution of potash dissolves pyroxylin by long standing in the cold, with phenomena of decomposition different from those produced when it is heated with a smaller excess of potash. The alkaline solution contains nitrite and a small quantity of carbonate of potash, and yields a pale yellow precipitate with acetate of lead

after supersaturation with acetic acid, and a further precipitate on the subsequent addition of basic acetate of lead. The first precipitate had, in one experiment, the composition of citrate of lead, but in another it yielded, by decomposition with sulphuretted hydrogen, an acid of the composition of tartrelic acid (x, 334). The precipitate produced by basic acetate of lead contained  $C^{12}H^6O^{15}, 7PbO$  (*tartersaures Bleioxyd*, therefore: van Kerckhoff). Hadow observed the evolution of ammonia on warming pyroxylin with potash-ley. In the cold there is slowly formed, without evolution of gas, a brown solution which reduces silver-salts and contains oxalic, nitrous, and nitric acid, together with a peculiar acid, Hadow's *pyroxylic acid*, which agrees in its properties to some extent with saccharic acid.—The alkaline solution of pyroxylin precipitates silver from an ammoniacal solution of silver, as a mirror on the sides of the vessel. (Vohl, *Dingl.* 112, 237).

15. Pyroxlin is completely converted into cotton-wool by alcoholic of *hydrosulphate of potassium* in the course of 24 hours. (Hadow, *comp.* p. 174).

16. A concentrated watery solution of *protochloride of iron* in excess acts upon pyroxylin, slowly in the cold, more quickly when heated, transforming it into ordinary cotton-wool. Ferrous acetate acts in the same way, but converts the nitrogen of the pyroxylin into ammonia, (Béchamp.) The regenerated cotton-wool has the composition and all the properties of the original cotton-wool, and may be again converted into pyroxylin and reduced a second time. (Béchamp, *comp.* also p. 173.)

17. Pyroxylin evolves all its nitrogen, in the form of nitric oxide, by contact with oil of vitriol and *metallic mercury*. (Crum.)

18. It is decomposed by boiling aqueous *permanganate of potash* with formation of nitric acid. (Cloeze & Buignet, *Compt. rend.* 47, 172; *J. pr. Chem.* 76, 501.)

19. With *common camphor*, *fat oils*, *wax*, or *resins*, pyroxylin forms dark brown solutions, which give off *nitrous acid*. (Hartig, *Untersuchungen über Schiessbaumwolle*, Braunschweig, 1847.)

*Combinations.* Pyroxylin is insoluble in water, and remains unchanged when boiled with water for a long time. (Pelouze.) After being kept for 5 weeks under water, it is found to be unaltered on drying (De Vrij; for decomposition by heating with steam, see p. 176).

It absorbs *fluoride of boron* without change of colour or loss of inflammability. If it contains unaltered cotton-wool, it explodes by contact with fluoride of boron. (Berthelot, *N. Ann. Chim. Phys.* 38, 58.)

Insoluble in aqueous *cuprammonia*. (Schlossberger, *J. pr. Chem.* 73, 573.)

Insoluble in glacial acetic acid. (Schönbein & Böttger, De Vrij.) Pyroxylin, prepared with nitrosulphuric acid diluted to a certain point, dissolves in glacial acetic acid. (Hadow; see p. 173.)—Forms, with *acetone*, a transparent jelly, which is curdled by water. With a large quantity of acetone, it forms a perfect solution. (De Vrij.)—Insoluble in *chloroform*. (Magnes-Lahens, *N. J. Pharm.* 16, 353.—Lepage, *J. Chim. méd.* 25, 147.)



Dissolves in *wood-spirit*. (Plessy & Schützenberger, *Mulhouse Soc. Bull.* 25, 187; *Dingl.* 131, 358.) — Insoluble in *alcohol*; slightly soluble in alcohol of  $40^{\circ}$ , according to Magnes-Lahens. — Vohl (*Ann. Pharm.* 70, 360) boiled pyroxylin, prepared by means of nitrosulphuric acid and insoluble in ether, for several hours with absolute alcohol, whereby it became soluble in ether. The alcohol had then in solution a substance which was deposited, on evaporation, in granular crystals, and possessed the following properties. It melted to an oil at  $70^{\circ}$  and solidified in the crystalline state on cooling; exploded under the hammer, or when heated to  $140^{\circ}$  or  $150^{\circ}$ ; and was obtained from solution in alcohol as a tough resin which gave off alcohol when heated with water. It dissolved in ether, only when it had absorbed alcohol; it was no longer soluble when freed from alcohol by precipitation from its alcoholic solution by water and boiling with water for several days. It dissolved in oil of vitriol, being reprecipitated by water; and in very strong boiling potash-ley, with evolution of ammonia. Its potash-solution reduced silver from an ammoniacal silver-solution. Hence Vohl assumes that alcohol extracts from pyroxylin a substance which incrusts the fibres, and so makes the residue soluble in ether.

Pyroxylin is insoluble in *ether*. With *ether-alcohol* it forms, according to its mode of preparation, sometimes a thick, viscid solution, sometimes a perfectly fluid one, and sometimes does not dissolve at all (comp. p. 170).

The solubility of pyroxylin was discovered by Fl. Domonte & Ménard, and nearly at the same time by Meynard & Béglow. The resulting solution, *collodion*, leaves the pyroxylin on spontaneous evaporation as a translucent, tenacious film (*collodion-film*) impervious to water.

To prepare collodion, Soubeiran (*N. J. Pharm.* 14, 263) shakes pyroxylin for a few minutes with 16 pts. ether and adds 1 pt. alcohol; Livonius (*N. J. Pharm.* 16, 122) employs 22 pts. ether and 4 pts. alcohol; Edwards, commercial ether of sp. gr. 0.7 to 0.76; Lassaigue *J. Chim. méd.* 24, 541), 20 pts. ether and 1 pt. alcohol of 90 p. c. — Berard (*Polyt. Centr.* 1858, 892) obtains dry, transparent, and durable collodion by digesting pyroxylin for a long time with warm ether-alcohol, decanting the clear solution after allowing it to settle, and distilling off the ether. The residue is completely soluble in ether-alcohol, and is not subject to spontaneous decomposition.

Collodion-film is inflammable. (Soubrisseau, *N. J. Pharm.* 14, 47.) The residue left by the evaporation of collodion gives off red fumes on drying (Domonte & Ménard), and sometimes explodes with violence at about  $115^{\circ}$  (*Compt. rend.* 23, 1088). A large quantity of water precipitates from the solution inflammable flocks of pyroxylin devoid of organised structure. (Domonte & Ménard, Magnes-Lahens.) The residue left by the evaporation of collodion is insoluble in water and in aqueous cuprammonia. (Schlossberger, *J. pr. Chem.* 73, 373.) Collodion does not become turbid when mixed with alcohol or ether (Mann), but solidifies after a time to a jelly if mixed with  $\frac{1}{2}$  or  $\frac{1}{4}$  pt. chloroform. Lessage, *J. Chim. méd.* 25, 147.)

Pyroxylin does not dissolve in ether containing from  $\frac{1}{2}$  to  $\frac{1}{4}$  pt. chloroform, in *nitric ether*, or in *monochlorinated vinic ether*. With *sulphovinic acid* and *oil of wine*, it forms slightly sticky solutions. (Magnes-Lahens.)

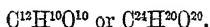
It dissolves in *methyl-acetic ether*, and in *acetic ether*. (Richier,

Schönbein & Böttger, Pelouze, comp. p. 173.) Pyroxylin swells up to a jelly in acetic ether, which leaves, by evaporation on glass plates, white pyroxylin devoid of organised structure, and this, when treated even with weak alcohol, loses acetic ether, and on drying remains behind as a powder. (Hartig.)—The solution is not sticky. (Magnes-Lahens, Livonius.)

Pyroxylin is insoluble in *oil of turpentine*. (Magnes-Lahens.)

Pyroxylin cannot be dyed, or only imperfectly. But pyroxylin which is partially decomposed by long keeping, or cotton-wool which is incompletely converted into pyroxylin by immersion in nitro-sulphuric acid, takes more brilliant colours when dyed than common cotton-wool. (Kuhlmann, *Compt. rend.* 42, 673 and 711).

## Tunicin.



C. SCHMIDT. (1845.) *Zur vergleichenden Physiologie der wirbellosen Thiere*, Braunschweig, 1845, 62; *Ann. Pharm.* 54, 318.—*J. pr. Chem.* 38, 433.

LÖWIG & KÖLLIKER. *J. pr. Chem.* 37, 439; *Compt. rend.* 22, 38.

DUMAS, EDWARDS, BOUSSINGAULT & PAYEN. *Compt. rend.* 22, 581; *Ann. Scienc. nat.* 1846, 238.

BERTHELOT. *Compt. rend.* 47, 227; *N. Ann. Chim. Phys.* 56, 149; *Rép. Chim. pure*, 1, 69; *J. pr. Chem.* 76, 371; *Pharm. Centr.* 1858, 675.

Discovered by C. Schmidt in 1846; distinguished from cellulose and named *Tunicin* by Berthelot.

*Occurrence.* *Comp. Handbuch*, viii. 473.—In the *Ascidiae* (Tunicata, *Lamark*); in the mantle of *Phallusia mamillaris*, and *Frustulia salina* (Schmidt), in all Tunicata (*Phallusia mamillaris*, *P. intestinalis*, *P. monachus*, *Cynthia papillata*, *Clavallina lepodiformis*, *Diozoma violacea*, *Botryllus Polycyclas*, *Pyrosoma gigantea*, *Sulpa maxima* [*Handb.* viii. *Zoochem.* 473]), not in the lower animals, as *Polypes*, *Medusae*, and *Mollusca* (Löwig & Kölliker); in the outer envelope of certain Tunicata (*Cynthia papillata*). (Berthelot.)

*Preparation.* The outer envelopes of the tunicata are treated successively with water, alcohol, ether, dilute acid and aqueous alkali (Schmidt), or they are boiled for some hours with concentrated hydrochloric acid, afterwards with aqueous potash of sp. gr. 1.28, then washed with water and dried. (Berthelot.)

*Properties.* White, translucent, very soft, with somewhat of a pearly lustre (Dumas, &c.), of the external unaltered form of the envelopes. (Löwig & Kölliker.) Tunicin prepared from *Phallusia mamillaris* forms an agglomerate of large shapeless cells. (Schmidt.)

				Schmidt.	
				<i>Phallusia mamillaris.</i>	<i>Frustulia salina.</i>
C <sup>24</sup> .....	144	.....	44.44	.....	46.19
H <sup>20</sup> .....	20	.....	6.17	.....	6.63
O <sup>20</sup> .....	160	.....	49.39	.....	47.18
<hr/>					
C <sup>24</sup> H <sup>20</sup> O <sup>20</sup> .....	324	.....	100.00	.....	100.00
<hr/>					
				Löwig & Kölliker.	Dumas, &c.
				<i>Phallusia mamillaris.</i>	<i>Cynthia papillata.</i>
C <sup>24</sup> .....	43.40	.....	43.20	.....	44.5
H <sup>20</sup> .....	5.68	.....	6.16	.....	6.4
O <sup>20</sup> .....	50.92	.....	50.64	.....	49.1
<hr/>					
C <sup>24</sup> H <sup>20</sup> O <sup>20</sup> .....	100.00	.....	100.00	.....	100.00

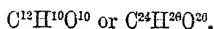
According to Schmidt, and Löwig & Kölliker, tunicin is cellulose or allied to cellulose; according to Berthelot, it is isomeric with cellulose and analogous to chitin. The envelopes treated with aqueous potash and then with hydrochloric acid, still contain from 3.2 to 3.8 p.c. nitrogen, but may be obtained free from nitrogen by treatment with 2 p.c. potash-ley, next with 25 p.c. potash-ley, and lastly with aqueous hydrochloric acid of the strength of 1 p.c. (Dumas, &c.)

*Decompositions.* 1. Tunicin heated in a glass tube is charred without losing its form, evolving the smell of burning vegetable tissue. Heated in the air it burns away quickly and completely.—2. Remains unaltered when heated with water to 200°. (Schmidt.)—3. It is coloured pale yellow when boiled with *alcoholic iodine*; if then moistened with oil of vitriol, it is coloured violet.—The violet colour is followed by solution of the tissue, which at the same time loses its colour, while a great number of yellow corpuscles, previously enclosed between the fibres, become visible under the microscope. (Dumas, &c.)—4. Not decomposed by boiling for several hours with dilute *nitric acid*. (Schmidt.)—5. Dissolves without coloration in cold oil of vitriol. (Dumas, &c.) The solution diluted with a large quantity of water contains, after an hour's boiling, a substance whose nature has not been determined, together with sugar, wherefore the solution neutralised with chalk, filtered and concentrated, reduces potassio-tartrate of copper, turns brown when boiled with potash, and ferments in contact with yeast, forming carbonic acid and alcohol. (Berthelot.)—6. Tunicin is not affected by dry *fluoride of boron*; with moist fluoride of boron it liquefies and then gives with water a solution which contains traces of sugar. (Berthelot.)—It remains unaltered by dilute *acids*, even when boiled with them for weeks, or by boiling *potash-ley*. (Berthelot.)

It dissolves slowly in concentrated *nitric acid*. (Schmidt.)—Dissolves with difficulty in aqueous *cuprammonia*. (Schlossberger, *J. pr. Chem.* 73, 374.)

Insoluble in *water*, *alcohol*, *glacial acetic acid*, or *ether*. (Berthelot.)

## Glycogen.



- CL. BERNARD. *Compt. rend.* 41, 461.—*Compt. rend.* 44, 578 and 1325; *J. pr. Chem.* 73, 251; abstr. *Kopp's Jahresber.* 1857, 552.—*Compt. rend.* 48, 77, 673 and 884.
- HENSEN. *Wörzb. medic. Verhandl.* 7, 219.—*Archiv. für pathol. Anatomie*, 9, 214; abstr. *Kopp's Jahresber.* 1857, 553.
- SANSON. *Compt. rend.* 44, 1159 and 1323; abstr. *Kopp's Jahresber.* 1857, 553.—*Compt. rend.* 45, 140 and 343.
- SCHIEFF. *N. Zeitschr. für phys. Heilkunde*, 1, 263.—*Compt. rend.* 48, 880.
- EUG. PELOUZE. *Compt. rend.* 44, 1321; *J. pr. Chem.* 73, 249; abstr. *Kopp's Jahresber.* 1857, 553.
- BONNET. *Compt. rend.* 45, 139 and 573; abstr. *Kopp's Jahresber.* 1857, 554.
- KEKULÉ. *Heidelb. naturw. Verhandl.* 1858, Jan.; *Chem. Centr.* 1858, 300; abstr. *Kopp's Jahresber.* 1858, 570.
- POGGIALE. *N. J. Pharm.* 34, 99; *Kopp's Jahresber.* 1858, 569.
- PAVY. *N. Phil. Mag. J.* 17, 142; *J. pr. Chem.* 77, 354; abstr. *Rép. Chim. pure*, 1, 236.
- GORUP BESANEZ. *Ann. Pharm.* 118, 227.

[The chemical nature of glycogen is treated of also *Handbuch*, viii. *Zoochem.* 74, 385 and 550.]

*Glykogen*, *Glykogensubstanz*, *thierisches Amylum*; *Matière amylacée*, *Glycogène*; *Hepatin*.—Discovered and investigated by Bernard.

*Occurrence.* In the liver. (Bernard.) In the placenta. (Bernard, *Compt. rend.* 48, 77 and 673.)—In the umbilical membrane of birds. (Serres, *Compt. rend.* 48, 86.) In graminivora, the liver generally contains glycogen, which is only found in the other organs, as in the muscular flesh of horses, when the animals have an abundance of food rich in starch. (Poggiale.—comp. *Handbuch*, viii. *Zoochem.* 385.)—In rabbits the liver contains as much as 2 p. c. of glycogen. (Kekulé.)

*Preparation.* 1. The liver of the quite freshly killed animal is cut into small pieces, immersed in boiling water, pounded and boiled for about an hour with a small quantity of water; the liquid is then strained off, the residue squeezed out, and the filtrate precipitated with 4 or 5 measures of alcohol of 38° to 40°. The yellowish white flocks are freed from sugar and soluble biliary matter by washing with a large quantity of alcohol; and from adhering nitrogenous substances, by boiling for  $\frac{1}{2}$  an hour to 1 hour, with concentrated potash-ley, whereby they are decomposed with evolution of ammonia; the solution is then mixed with a small quantity of water, filtered, and precipitated with 4 or 5 measures of alcohol of 38° or 40°. The precipitate is freed from potash by washing with a large quantity of alcohol; it is then dissolved in a small quantity of water, the solution neutralised with acetic acid, and again precipitated with alcohol. Purer glycogen is thus precipitated, while

acetate of potash remains in solution. (Bernard.) So prepared, it is apt still to contain lime-salts, which may be removed for the most part by repeated solution in strong acetic or cold dilute nitric acid, and precipitation with alcohol. (Kekulé. — comp. Hensen, *Handbuch*, viii. *Zoochem.* 385.)

2. The fresh, filtered, and cooled decoction of the liver is precipitated with glacial acetic acid, whereupon nearly pure glycogen is thrown down, the albuminous substances remaining in solution. (Bernard.)

3. If the liver is washed out with cold water, by inserting the nozzle of a caoutchouc syringe into the *vena porta* and driving a stream of cold water through the capillaries by careful pressure, a blood-red liquid is first obtained, then a bright rose-coloured liquid, then a milky liquid, and at last water. The rose-coloured and milky liquids are heated to boiling and the filtrate precipitated with 2 measures of alcohol of 90°; and the flocks are collected after some hours, washed with alcohol, dissolved in water containing acetic acid, and again heated to boiling. The filtrate precipitated a second time with alcohol, yields flocks of glycogen in abundance, which must be freed from fat by washing with ether and dried in vacuo. (Gorup-Besanez.)

*Properties.* White, mealy powder, which even under the microscope shows no peculiar form. Without smell. Tastes like starch. Neutral. (Bernard and others.)

Calculation according to Pelouze.				Calculation according to Kekulé.				Gorup- Besanez.	
Pelouze.				Kekulé.				at 100°.	
12 C	72	40.00	39.8	12 C	72	44.44	44.49	44.50	
12 H	12	6.67	6.1	10 H	10	6.17	6.49	6.38	
12 O	96	53.33	54.1	10 O	80	49.39	49.02	49.12	
$C^{12}H^{12}O^{18} 180$				$C^{12}H^{10}O^{10} 162$				100.00	
	100.00	100.0			100.00	100.00	100.00	100.00	

Loses 1 at. water at 100°. (Pelouze.) — See *Handbuch*, viii, *Zoochem.* 385, for Schiff's and for Sanson's statements respecting the identity of glycogen with inulin and dextrin. Lochner (*Dissert.* Erlangen, 1858), obtained numbers corresponding to the formula  $C^{12}H^{12}O^{18}$ , 2 HO. On account of the discrepancy between the several statements, Gorup-Besanez thinks it possible that various kinds of glycogen may be obtained from the liver.

*Decompositions.* 1. All reagents which transform starch into sugar, similarly change glycogen, first into a substance corresponding to dextrin, then into sugar. (Bernard.) The sugar so produced is identical with grape-sugar. (Berthelot & de Luca, *Compt. rend.* 49, 213.) This transformation is occasioned by dilute mineral acids, diastase, and the ferments contained in the blood, saliva, liver, and pancreas. (Bernard.) Boiling dilute sulphuric acid first clarifies the aqueous solution, and only produces sugar after continued boiling. (Kekulé.) — Neutral aqueous glycogen is immediately converted into sugar by saliva; the transformation takes place very slowly, or not at all, in presence of free acid, caustic or carbonated alkalis. (Pavy.) If the glycogen

contained in a concentrated decoction of liver or muscular flesh is warmed with saliva, it ferments on the subsequent addition of yeast. (Poggiale.) Glycogen which has not undergone this preliminary treatment, does not ferment on addition of yeast. (Bernard.)

2. By *roasting*, glycogen is converted into a substance similar to dextrin. (Bernard.) The dextrin formed thus, or according to 1, rotates the plane of polarisation towards the right, does not reduce an alkaline solution of cupric oxide, is not coloured blue by iodine, and does not ferment with yeast. It gives a clear solution with water, not with strong alcohol. (Bernard.)

3. Yields xyloidin when treated with concentrated *nitric acid*; and oxalic acid when boiled with dilute nitric acid. (Pelouze.) If concentrated nitric acid is poured over glycogen dried at  $100^{\circ}$ , solution takes place after a few moments, and, if water is immediately added, a quantity of xyloidin is obtained amounting to 130 p. c. on the glycogen employed. If the nitric acid solution is allowed to stand for some time, water precipitates a smaller quantity of xyloidin, and after several days none at all. (Pelouze.)—4. Glycogen does not reduce an alkaline solution of *cupric salts*. (Bernard.)

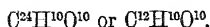
*Combinations.* Glycogen forms an opalescent solution with *water*. (Bernard, Kekulé.)—In the absence of ferments, the solution undergoes no spontaneous alteration on standing. (Bernard.) On evaporating the solution, the glycogen separates out in films. (Hensen.) According to Bernard and Lehmann, the solution is precipitated by *acetic acid*, according to Lochner and Gorup-Besanez, it is not precipitated by acetic acid, but is rendered clearer by it, according to Gorup.

*Iodine* colours it violet or bright brown-red, seldom pure blue (Bernard), violet or oftenest red-brown. (Kekulé.)

It is precipitated from solution in water by *basic acetate of lead* (Bernard); not precipitated. (Hensen.)

It is quite insoluble (Bernard), slightly soluble (Hensen) in *alcohol*.—*Animal charcoal* precipitates it from solution in water. (Bernard.)

## Dextrin.



BIOT & PERSOZ. (1833.) *Ann. Chim. Phys.* 52, 72; *Schw.* 66, 169; *Pogg.* 32, 160; *Ann. Pharm.* 6, 209.

PAYEN & PERSOZ. *Ann. Chim. Phys.* 53, 73; *Pogg.* 32, 182.—*Ann. Chim. Phys.* 56, 337.

PAYEN. *J. Chim. méd.* 9, 504, 549, and 572.—*Ann. Chim. Phys.* 61, 372; 65, 225, and 234.—*N. Ann. Sc. nat. Botan.* 10, 85, and 170.

GUÉRIN-VARRY. *Ann. Chim. Phys.* 60, 68.

JACQUÉLAIN. *N. Ann. Chim. Phys.* 8, 255; *J. pr. Chem.* 30, 477.

BÉCHAMP. *Compt. rend.* 51, 256.

*British gum*; *Amidine* (Chevreul.), *Gomme amidone*, *Gomme dextrine* (Payen & Persoz), *Dextrine* (Biot), *Leiocomme*, *Stärkegummi*, *Dextringummi*.—Béchamp distinguishes between *dextrine de fécule* and *dextrine de ligneux*.

As early as 1811, Vauquelin (*Bull. Pharm.* 3, 54) mentioned roasted starch, which Döbereiner subsequently (*Schw.* 8, 207) regarded as gum; Biot & Persoz, as the contents of the starch-granules (Chevreul's *amidine*). Payen & Persoz recognised it as a product of the transformation of the amidon contained in the starch-granules. According to Chevreul (1834) it is identical with Couverchel's *gomme normale*, Caventou's *amidon modifié*, Guibourt's *amidon soluble* or *amidine*. — It has been examined chiefly by Payen. — It was named dextrin and distinguished from gum, by Biot & Persoz, on account of possessing a rotatory power towards the right; but, according to Béchamp (*N. Ann. Chim. Phys.* 48, 461), Biot's original dextrin is not the same as the substance to which that name is now given, but is identical with Béchamp's soluble starch (p. 102). According to Sanson (*Handbuch*, viii, *Zoochem.* 550), dextrin is identical with glycogen. [According to Eug. Pelouze (*Compt. rend.* 44, 1321), the substance regarded as dextrin or glycogen by Sanson is an altered albuminous body.—W.]

*Occurrence.* Probably in nearly all vegetable juices, but mistaken for gum (Mulder, *Lehrb. d. phys. Chem.* 232), not in cereal grains. (Mitscherlich, *Lehrb.* 368.) In rye and wheat (Fürstenberg, *J. pr. Chem.* 31, 195); probably in *Fucus saccharinus* (Witting, *J. pr. Chem.* 73, 138); in Spanish chestnuts to the extent of 22·8 to 23·3 p. c. (Albini, *Wien. Acad. Ber.* 13, 502); in the blood (*Handbuch*, viii, *Zoochem.* 387 and 550); in the juice of flesh (*ibid.* 387 and 550); in the lungs and spleen. (*ibid.* 387.) — In bread, beer, and other articles of food, as a product of the metamorphosis of starch.

*Formation.* A. From starch (comp. pp. 81, 84–86, 90, &c.) 1. By roasting until the starch acquires a yellowish brown colour and evolves vapour. (Döbereiner; Bouillon-Lagrange, *Bull. Pharm.* 3, 395.) By heating to 200° or 210°. (Payen.) The presence of water is unnecessary or even disadvantageous, for starch dried at 150° yields scarcely anything but dextrin when heated for  $\frac{1}{2}$  hour to 210° or 214° in an oil-bath, whereas air-dried starch forms soluble starch at the same time. (Maschke, *J. pr. Chem.* 61, 1.) — 2. By several days' heating to 100° with water (only traces are formed by using 2, or from 30 to 40 measures of water). (Maschke.) By heating with water to 150° (Mitscherlich, *Pogg.* 55, 221), under increased pressure (Jacquelin, *Ann. Chim. Phys.* 73, 187).

3. By the action of acids, as of cold oil of vitriol (Payen), or of dilute sulphuric acid at 85°. It is formed more quickly and at a lower temperature by the action of strong than by that of very dilute sulphuric acid; by continued boiling of the mixture it is transformed into glucose. (Biot & Persoz.) By dilute nitric acid. (Biot & Persoz, Payen.) By heating with  $\frac{1}{2}$  pt. tartaric acid and 5 pts. water to 125° for an hour in a Papin's digester. (Payen, *J. Pharm.* 7, 267.)

4. By digestion with aqueous alkali. (Payen.)

5. By the action of diastase at 60° or 75°. (Payen & Persoz, Guérin-Varry.)

6. By the action of sun-light on starch-paste. (St. Victor & Corvisart, *Compt. rend.* 49, 368; *Ann. Pharm.* 113, 112.)

In the modes of formation 1 to 3, the formation of dextrin is preceded by that of soluble starch. Comp. pp. 82, 84, and 102. (Maschke, Béchamp.) Sugar is formed at the same time as dextrin in processes 3 to 5. (Musculus. — Comp. pp. 85, 90, and 91.) — According to Delifs

(*Pogg.* 109, 648), dextrin differs in its properties according as it is prepared with malt, with dilute sulphuric acid, or by roasting.

B. *From Cellulose.* By the action of oil of vitriol. (Braconnot, *Ann. Chim. Phys.* 12, 172.) — The *dextrine de ligneux* so obtained possesses most of the properties of *dextrine de fécule*, but has a different rotatory power, and forms a *dextrine nitrique ligneux* which differs from binitrodextrin. (Béchamp.) — According to Mulder, the dextrin of vegetable juices is formed from cellulose or a similar substance under the influence of diastase, and is further transformed into starch and sugar.

*Preparation.* 1. Starch is heated in a shallow vessel with a double bottom (the intermediate space being filled with heated oil) to 150—160°, with continual stirring, until it begins to turn yellow and becomes soluble in water. (*British gum*, or *Leiocomme* of commerce.) — In order to purify it, it is repeatedly washed with cold and hot alcohol of sp. gr. 0·843; dissolved in water at 90°, and precipitated with alcohol; the precipitate again dissolved in hot water, and the filtered solution evaporated to dryness. (Payen.) — 2. One part of starch is acted upon with  $\frac{1}{4}$  pt. oil of vitriol and 2·8 pts. water. The acid is mixed with part of the water and the starch stirred up with the rest; the diluted acid is gradually poured upon the starch, and the mixture is kept for some time at 90°. The dextrin is precipitated by alcohol from the clarified solution. (Biot & Persoz.) — Dextrin so prepared cannot be purified from sugar which is formed at the same time and adheres to it, except by dissolving it at least ten times in water and precipitating the solution with alcohol, which should not be employed in excess. (Payen.) — The solution obtained by boiling starch with acid contains, immediately after it has become clear, but little dextrin, but a large quantity of soluble starch. (Maschke, *J. pr. Chem.* 61, 1.) — Hofmann (*Dingl.* 149, 320; *Chem. Centr.* 1859, 509; *N. Br. Arch.* 98, 110), exposes corn with 1·5 pt. water and 0·01 to 0·02 pt. oil of vitriol to high-pressure steam at 107°—149°, for 2 or 3 hours, in an air-tight mash-tun, pours off the liquid, saturates it with chalk, and, after allowing the precipitate to settle, decants and evaporates to dryness. — 3. Starch is moistened with 0·002 pt. nitric acid and the requisite quantity of water, formed into cakes which are broken up after being allowed to dry in the air, spread out in shallow layers in a chamber supplied with hot air, gradually heated to 80°, and at last dried at 110°. (Payen.) — 4. Starch is digested for 12 hours at 50°—60° with 5 p. c. potash- or soda-ley; the clear solution is neutralised with acetic acid, and precipitated with alcohol. Purification as in 2. (Payen.)

5. Five parts of sprouted barley-malt with 400 pts. water at 25°—30° are slowly heated to 60°, 100 pts. starch are added, and the mixture is kept at 65°—75° for about  $\frac{1}{2}$  an hour, or until the liquid, which is at first milky, has become clear and perfectly fluid, it being kept stirred all the time; the temperature is then quickly raised to 95° or 100°, to destroy the activity of the diastase; the solution is filtered when cold and already clarified by subsidence; and the filtrate evaporated at 110°, the scum which forms on the surface being skimmed off, to a syrup which solidifies to a jelly on cooling, and is then divided into thin layers and dried in a current of air in a drying oven. The product is purified by precipitating the concentrated aqueous solution with alcohol, treating the precipitate, which consists of dextrin with a



small quantity of starch, with water, which dissolves the dextrin, and again precipitating with alcohol. (Payen & Persoz.)—Sprouted barley-malt may also be mixed with 7 pts. water and gradually heated in the water-bath to  $65^{\circ}$ , with constant stirring; then to  $75^{\circ}$  for 25 minutes;  $\frac{1}{10}$  pt. animal charcoal added; the liquid filtered, warmed in the water-bath to  $60^{\circ}$ , and starch added to it as above. The dextrin thus obtained is very white.

In order to obtain dextrin-syrup, twice the quantity of malt indicated above must be used, and the mixture must be digested between  $65^{\circ}$  and  $75^{\circ}$  for a longer time, until it is no longer coloured blue by iodine. (Payen.) The dextrin-syrup so obtained is precipitated with alcohol of 95 p. c., and filtered; the residue is dissolved in 8 pts. water at  $75^{\circ}$ ; the solution is shaken with animal charcoal for a quarter of an hour, and filtered; and the filtrate is evaporated in vacuo. (Guérin-Varry.)—Starch is digested at  $70^{\circ}$ — $75^{\circ}$  with 0.02 pt. diastase and 5 pts. water, until the liquid is no longer coloured blue by iodine; it is then filtered, and evaporated; the residue freed from sugar by exhaustion with alcohol of 85 p. c., then dissolved in spirit of 30—35 p. c.; and the solution filtered from the undissolved starch is evaporated. (Payen & Persoz.)

*Properties.* Solid, brittle, colourless or slightly coloured, transparent, gummy mass, reducible by trituration to a white powder which grates between the fingers, (Payen. *J. Chim. méd.* 21, 427), sp. gr. 1.52. (Payen.)—Tasteless (Payen, Guérin-Varry), has a sweetish gummy taste, (Bouillon-Lagrange); inodorous, permanent in dry air, and at  $100^{\circ}$  (Guérin-Varry).—Specific rotatory power  $[\alpha] = 138.7^{\circ}$  to the right,  $= 176^{\circ}$  (Béchamp). Rotatory power of *Dextrine de Ligneux*  $[\alpha] = 88.9^{\circ}$  to the left. (Béchamp.)—Neutral.

<i>In vacuo.</i>			Payen & Péligot.		
24 C .....	144	.....	44.44	.....	43.31
20 H .....	20	.....	6.17	.....	6.60
20 O .....	160	.....	49.39	.....	50.09
$C^{24}H^{20}O^{20}$ .....	324	.....	100.00	.....	100.00

Payen.						
	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>	<i>e.</i>	
24 C .....	42.54	.....	43.63	.....	43.27	44.18
20 H .....	6.22	.....	6.00	.....	6.11	6.00
20 O .....	51.24	.....	50.37	.....	50.62	49.82
$C^{24}H^{20}O^{20}$ .....	100.00	.. 100.00	100.00	.....	100.00	100.00

*a.* dried at  $80^{\circ}$ ; the other products at  $100^{\circ}$  in vacuo (Payen.)

*a.* and *b.* prepared by (1); *c.* from commercial dextrin and purified as in (1); *d.* prepared from starch with cold oil of vitriol; *e.* by (4).

*Decompositions.* 1. Dextrin heated to  $120^{\circ}$ — $130^{\circ}$  becomes pale yellow, gives off water, and acquires the smell of toasted bread; after half-an-hour's heating to  $145^{\circ}$ — $150^{\circ}$ , it assumes a deeper yellow colour; after an hour's heating to  $195^{\circ}$ — $200^{\circ}$ , it becomes reddish without melting or losing its transparency; at  $225^{\circ}$ , it begins to melt, and at  $235^{\circ}$ , it swells up strongly, turns yellowish brown, and yields

acetic acid, carbonic acid, carburetted hydrogen and other products. (Guérin-Varry).—When thrown on red-hot coals, it burns like gum (Bouillon-Lagrange).—2. Treated with *nitric acid*, it yields oxalic acid (Bouillon-Lagrange, Fürstenberg), no mucic acid (Guérin-Varry), probably also saccharic acid (Gerhardt, *Traité* 2, 493).—3. With *nitro-sulphuric acid*, it forms binitrodextrin (Béchamp).—4. With *oil of vitriol*, it blackens and gives off acetic acid (Bouillon-Lagrange); boiled with 4 pts. water and 0.01 oil of vitriol, it forms glucose (Payen & Persoz).—It is converted into sugar by boiling with any dilute acid (Biot & Persoz).—5. It is not altered by *hydrochloric acid*.—6. Heated to 100° for 50 or 60 hours with *glacial acetic* or *butyric acid*, it gives off water, and forms a small quantity of a compound analogous to or identical with aceto- or butyro-glucose (Berthelot, *N. Ann. Chim. Phys.* 60, 98).—7. Heated with aqueous bicarbonate of potash and *iodine*, it yields iodoform (Millon, *Compt. rend.* 21, 828; *J. pr. Chem.* 37, 55).—8. It is not altered by aqueous *permanganate of potash* (E. Monier, *Compt. rend.* 46, 425; *J. pr. Chem.* 73, 479).—9. Heated to 150° in a sealed tube with strong *caustic ammonia*, it behaves like starch (p. 87), but the substance thus obtained by continuing treatment for 7 days, contains 11 p.c. nitrogen (Schützenberger, *Zeitschr. Ch. Pharm.* 4, 66).—10. It colours a *cupric solution containing caustic potash* blue, but does not throw down cuprous oxide from it till heated to 85°, and even then but slowly (Trommer, *Ann. Pharm.* 39, 360; Delffs); not even when heated (Fürstenberg, *J. pr. Chem.* 31, 195).—11. Heated with *cinchona bases*, it gives off red vapours which condense to a red liquid (Batka, *Chem. Centr.* 1859. 865).—12. It does not ferment with water and *yeast* (Biot & Persoz, Guérin-Varry, Payen); in contact with water and *calves rennet*, at 40°, it is converted into milk-sugar or a modification thereof (Frémy, *J. Pharm.* 25, 299). By water and *dias-tase* at 60°—70°, it is gradually converted into sugar (Payen & Persoz), but only partially (Guérin-Varry). See the statements of Musculus, (p. 91).

*Combinations. With Water.* Dextrin exposed to moist air absorbs 4 at. water, of which it gives off 2 at. in vacuo at 15°, and the rest between 100° and 140°. (Payen.)

It deliquesces to a syrup in air saturated with moisture, and dissolves readily in water. (Biot & Persoz.) The solution is clear and gummy (Bouillon), glutinous (Biot & Persoz), and is precipitated by water (Guerin-Varry). For the rotatory power *vid. sup.*

Aqueous dextrin does not suffer any alteration of rotatory power by keeping (Biot & Persoz), but loses it to a certain extent when heated (Dubrunfaut, *Compt. rend.* 23, 43).—When kept, even out of contact with the air, it deposits pulverulent modified dextrin (Biot & Persoz); when frozen it deposits a powder which redissolves on thawing (Jacquelin, *Ann. Chim. Phys.* 73, 187). Aqueous dextrin is not coloured by aqueous solution of *iodine* (Payen, Guerin-Varry); it is coloured wine-red (Biot & Persoz); purple-red if the dextrin has been prepared by heating 1 pt. of starch with 5 pts. water in a Papin's digester, for  $\frac{1}{2}$  to  $\frac{3}{4}$  of an hour,—not at all if prepared by heating in like manner for 2 hours. Also by treating starch with oxalic acid and water to 130° for an hour, neutralising the solution with chalk, and repeatedly precipitating the dextrin from its solution by alcohol, a dextrin is obtained which is coloured purple-red by iodine-water, whereas the dextrin obtained by heating in like manner for 2 hours is not coloured by iodine-water. (Jacquelin, *Ann. Chim. Phys.* 73, 187; see also Delffs, *Pogg.* 109, 648.)

*With Metallic oxides.*—Metallic oxides insoluble in water generally dissolve, as double compounds, in aqueous dextrin, in presence of a slight excess of potash.

*Barium-compound.*—Precipitated from a solution of dextrin in alcohol of 56 p. c., or of wood spirit 50 p. c., saturated at  $24^{\circ}$ , on addition of a nearly saturated solution of hydrate of baryta in wood-spirit. The precipitate is washed with weak wood-spirit, and dried in vacuo or in air free from carbonic acid. (Payen.) The aqueous solution of dextrin prepared by roasting precipitates baryta-water; that which is prepared with sulphuric acid or malt does not. (Delfs.)

					Payen.
2 BaO .....	153	...	29.9	.....	31.8
$C^{24}H^{18}O^{18}$ .....	306	...	70.1		
<hr/>					
$C^{24}H^{18}Ba^2O^{20}$ .....	459	...	100.00		

*Lead-compound.*—The solution of dextrin in water or weak spirit is not precipitated by either neutral or basic acetate of lead. (Payen.) Basic acetate of lead added in excess to a very concentrated solution of dextrin, throws down a gelatinous precipitate. (Stadeler, *Ann. Pharm.* 111, 26.) A solution of basic acetate of lead is precipitated by dextrin prepared with malt, but not by dextrin prepared from starch by roasting or by the action of sulphuric acid. (Delfs, *Pogg.* 109, 648.)

*a. Basic.* A solution of dextrin is poured into an excess of an ammoniacal solution of neutral acetate of lead, and the precipitate is washed and dried at  $50^{\circ}$  in vacuo. Loosely coherent white powder, which, when heated in vacuo to  $180^{\circ}$ , gives off water and turns yellow. Soluble in acetic acid. (Payen.)

					Payen.	
<i>In vacuo.</i>					<i>at 50°.</i>	<i>at 80°.</i>
24 C .....	144.0	...	19.1	...	18.5	19.0
18 H .....	18.0	...	2.4	...	2.7	2.4
18 O .....	144.0	...	19.2	...	21.0	19.4
4 PbO .....	446.8	...	59.3	...	57.8	59.2
<hr/>						
$C^{24}H^{18}Pb^2O^{20}, 2PbO$ .....	752.8	...	100.0	...	100.0	100.0

*b. Bibasic.* A cold solution of neutral acetate of lead mixed with ammonia is added by drops to an excess of a warm solution of dextrin, till the precipitate, which at first disappears on stirring, encloses about half the dextrin present. This precipitate is washed in an apparatus which protects it from the action of carbonic acid, and dissolved with aid of heat (in acetic acid? Kr.); the solution evaporated in a retort till the boiling point rises to  $115^{\circ}$ , then cooled, and precipitated with excess of ammonia; and the precipitate is collected, washed and dried. (Payen.)

					Payen.
<i>at 100°.</i>					
2PbO .....	223.4	.....	42.2	.....	40.1
$C^{24}H^{18}O^{18}$ .....	306.0	.....	57.8		
<hr/>					
$C^{24}H^{18}Pb^2O^{20}$ .....	529.4	.....	100.0		

*c. Acid?* If the liquid which remains after precipitation of *b* be

mixed with alcohol, the resulting precipitate contains 10·17 per cent. of lead. (Payen.)

An aqueous solution of dextrin is not precipitated by *ferrous sulphate* (Payen); it does not decolorise aqueous ferricyanide of potassium mixed with  $\frac{1}{2}$  pt. hydrate of potash, even on boiling (Gentele, *Dingl.* 152, 68); neither does it precipitate *mercurous nitrate* or *protochloride of tin* (Payen). Dextrin prepared with malt or by roasting throws down, white precipitate from mercurous nitrate, that which is prepared with dilute sulphuric acid does not. (Delffs, *Pogg.* 109, 648.)

Aqueous dextrin dissolves *glucose*; the solution reduces a cupric solution containing potash, without previous blueing (Ventzke, *J. pr. Chem.* 25, 81).

Dextrin is insoluble in *alcohol* of sp. gr. 0·837 or 0·88 either cold or boiling; but abstracts from it at the boiling heat a certain quantity of water, and softens. When covered with 1000 pts. of alcohol of sp. gr. 0·91, it does not dissolve completely even on boiling, but the same alcohol in contact with a larger quantity of dextrin, dissolves the greater part of it at the boiling heat, amounting to 3 p. c. of its own weight, and deposits it partly again on cooling, so that after six days the quantity still remaining in solution amounts to  $\frac{1}{16}$  per cent. of the alcohol.

According to Payen, it dissolves readily in alcohol of 30 p. c., less easily in alcohol of 45, not at all in alcohol of 80 p. c., and is precipitated as a syrup by alcohol of 84 p. c. from its solution in weaker alcohol. — Anthon found that when dextrin prepared with malt was boiled with 143 pts. alcohol of sp. gr. 0·95, the whole dissolved, but half of it separated on cooling, whereas the same dextrin boiled with 3 pts. alcohol, likewise dissolved and separated on cooling, to such an extent only that 19 per cent. remained in solution. Hence Anthon regards this dextrin as decomposable by alcohol of sp. gr. 0·95 and the portion which separates on cooling as different from that which remains dissolved.

Dextrin is soluble in *methylic alcohol*. — The solution mixed with an equal quantity of water is not precipitated by common alcohol of 56 per cent. (Payen.)

Insoluble in *ether*. (Guérin-Varry.)

### *Appendix to Dextrin.*

#### 1. Pyrodextrin.

GÉLIS (1857). *N. Ann. Chim. Phys.* 52, 388; *N. J. Pharm.* 33, 405; abstr. *Compt. rend.* 45, 991; *Chem. Centr.* 1858, 164.

*Formation and Preparation.* By the roasting of starch (appearing, indeed, to be the only coloured substance thereby produced), of cereal grains, potatoes, maize, or coffee. — Starch is heated, with constant stirring, in an open vessel strongly heated on one side, fresh portions being continually brought in contact with the hot part, till it is free from adhering water, swells up strongly, gives off pungent vapours, and sinters together, so that it is easily separated from the hot bottom of the vessel. It is dissolved in hot water; the clear filtrate evaporated, and the residue dried and heated by small portions in an

air-bath to  $220^{\circ} - 230^{\circ}$ , to complete the roasting. The spongy product thus obtained is purified, especially from adhering dextrin, by repeatedly dissolving it in water and precipitating the solution with alcohol, as long as dark flakes continue to separate—or, in presence of a large quantity of dextrin, by precipitating the aqueous solution with excess of baryta-water containing alcohol, washing the resulting precipitate with weak spirit, pouring upon it a quantity of sulphuric acid sufficient to decompose it, filtering the liquid to remove sulphate of baryta, and precipitating the filtrate with alcohol. The pyrodextrin, which separates in the form of syrup, is dissolved in a small quantity of water, the filtrate evaporated over the water-bath, and the residue dried at  $140^{\circ}$ .

*Properties.* Solid, brown, friable mass, shining and tough when moist. Inodorous and tasteless.

				Gélis. at $160^{\circ}$ .
96 C.....	576	.....	46.37	..... 45.71
74 H .....	74	.....	5.95	..... 6.20
74 O .....	592	.....	47.68	..... 48.09
<hr/>				
$C^{96}H^{74}O^{74}$ .....	1242	.....	100.00	..... 100.00

According to Gélis, it is  $C^{48}H^{37}O^{37} = 4C^{12}H^9O^9 + HO$ .

*Decompositions.* 1. Remains unaltered at  $210^{\circ} - 220^{\circ}$ , but decomposes at a higher temperature; takes fire with difficulty, and leaves a hard, coherent, slowly-burning cinder.—2. Treated with *nitric acid*, it yields oxalic acid.—3. By *oil of vitriol* or strong *hydrochloric acid*, it is converted into a sparingly soluble brown powder; dilute sulphuric or hydrochloric acid alters it but very slowly, even when heated.—4. It reduces cuprous oxide from an *alkaline solution of cupric oxide*, and from solutions of *gold-* and *silver-*salts, it reduces the metals.

*Combinations.* Pyrodextrin when exposed to the air takes up 3 at. water, and afterwards dissolves readily in water forming a brown adhesive gum.

Aqueous pyrodextrin is not coloured purple-red by *iodine* (like dextrin), but is decolorised by moist hydrate of alumina.

*Barium-compound.*—Obtained by precipitating aqueous pyrodextrin with baryta-water, washing the precipitate with weak alcohol, and drying it in a space free from carbonic acid. Sparingly soluble in water, soluble in glacial acetic acid.

				Gélis.
96 C .....	576	....	37.64	.... 36.92
72 H .....	72	....	4.70	.... 4.90
72 O .....	576	....	37.64	.... 37.98
4 BaO .....	306.4	....	20.02	.... 20.20
<hr/>				
$C^{96}H^{72}Ba^4O^{76}$ .....	1530.4	....	100.00	100.00

*Lead-compounds.* Pyrodextrin forms several compounds with oxide

of lead. The *neutral compound* is obtained by mixing aqueous solutions of pyrodextrin and neutral acetate of lead, and precipitating the mixture with absolute alcohol, or better, by precipitating a concentrated aqueous solution of pyrodextrin with excess of neutral acetate of lead dissolved in alcohol; dissolving the black semifluid precipitate several times in water and precipitating with alcohol; and lastly, evaporating the aqueous solution of the salt so purified, first on a water-bath, then in a drying-oven.

Very soluble in water, easily precipitated therefrom by alcohol. Not affected by the carbonic acid of the air.

					Gélis.
96 C .....	576.0	....	39.81	....	39.09
72 H .....	72.0	....	4.97	....	5.21
72 O .....	576.0	....	39.81	....	40.50
2 PbO.....	223.4	....	15.41	....	15.20
<hr/>					
C <sup>96</sup> H <sup>72</sup> Pb <sup>2</sup> O <sup>74</sup> .....	1447.4	....	100.00	....	100.00

Pyrodextrin is sparingly soluble in alcohol of 22 p. c.; insoluble in *absolute alcohol* and in *ether*. (Gélis.)

### *Carbo-hydrates* C<sup>12</sup>H<sup>11</sup>O<sup>11</sup>.

The extensive group of amorphous vegetable substances, formerly designated by the common name of *gum*, which form with water a viscid and glutinous solution, and are precipitated or coagulated by alcohol, has been separated by Fourcroy, Thomson, Guérin-Varry, and others, into several smaller groups, each of which however includes a number of bodies differing from one another in origin or in mode of formation. In the majority of cases, the existing observations are not sufficient to enable us to decide with certainty on the identity or difference of the individual members of these groups, especially as the great mass of observations have hitherto been made on the gums as they occur in nature (mixtures of several distinct gums or containing inorganic impurities). On the authority of the researches of Neubauer, Fremy, and others, the following substances are here treated as definite chemical compounds: 1. *Arabic acid*, with reference to the researches on gum-arabic. — 2. *Metagummic acid*, including cherry tree gum. (Guérin-Varry's Cerasin.) — 3. *Bassorin*. — 4. *Vegetable mucus*, regarded by most authors as identical with bassorin, but differing therefrom in its mode of occurrence in a manner which renders it probable that the two are chemically different.

Fourcroy distinguished *Gum-arabic*, *Gomme du pays*, and *Gum-tragacanth* without however precisely characterising these divisions. — Thomson (in his "System of Chemistry," 4, 21), made four divisions: 1. *Gum*, in which term he included gum-arabic, gum-senegal, and the gum of *Stertulia urens*, precipitable by solution of silica. — 2. *Mucilage*, including that from linseed, quinces, and marsh-mallow roots, not precipitable by solution of silica (Guérin-Varry). — 3. *Cerasin*, including the gums indigenous in Europe. — 4. *Gum-tragacanth*. — Vauquelin made a special division for *Bassorin*, on account of its insolubility in water. — Dextrin and other products resulting from the decomposition

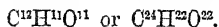
of starch and woody-fibre, were formerly classed among the gums, till Biot distinguished dextrin therefrom, on account of its action on polarised light.

Guérin-Varry regards as characteristic of gum, the capability of forming mucic acid with nitric acid. His classification distinguishes:

1. *Arabin*, soluble in water. — 2. *Bassorin*, insoluble in water. — 3. *Cerasin*, likewise insoluble in water, but converted into arabin by boiling with water. Guibourt distinguishes several subdivisions. Berzelius (*Lehrbuch*, 3 Aufl. 6, 396) distinguished two classes of gums: 1. *True gum*, soluble in water, either cold or boiling, to a thick, glutinous liquid, insoluble in alcohol, precipitable by basic lead-salts, but not by tincture of galls, mostly converted by nitric acid into mucic acid. — 2. *Vegetable mucus*, perfectly insoluble in cold, soluble for the most part in boiling water, in which it swells up to a thick mucilage, not precipitable by solution of borax or tincture of galls.

Gum-arabic was shown by Neubauer to consist of the potash- and lime-salts of a peculiar substance, *arabin* (arabic acid, according to Hekmeljer), either of acid nature or related to the acids. Arabin is  $C^{12}H^{11}O^{11}$  or  $C^{24}H^{22}O^{22}$ , and is capable of forming with lime a compound identical with gum-arabic. Neubauer observed that arabin after drying merely swells up in water without dissolving, but that its solubility is restored by addition of bases. Gum-arabic undergoes a similar alteration when its highly concentrated aqueous solution is poured upon the surface of oil of vitriol, or when it is roasted with oxalic acid (Freymy), or heated for some time to  $150^{\circ}$  (Gélis), being converted, by the former treatment, into Freymy's metagummic acid; by the latter into Freymy's metagummate of lime, Gélis's artificial cerasin. The portion of cherry tree gum (Guérin-Varry's cerasin), which is insoluble in water, is, according to Freymy and Gélis, metagummate of lime, and, like that substance, convertible into gummate of lime. The portions of Bassora gum, insoluble in water, yield, under the influence of alkalis, a product different from gummate of lime, but likewise soluble in water. (Freymy.)

### Arabic Acid and Gum-arabic.



CRUIKSHANK. *Scher. J.* 3, 289.

BOSTOCK. *N. Gehl.* 8, 573,

VATQUELIN. *Ann. Chim.* 6, 178; 54, 312; 80, 315. — *Bull. Pharm.* 3, 49.

PFÄFF. *System d. Mat. med.* 1, 102.

BERZELIUS. *Ann. Chim.* 95, 77.

TROMMSDORFF. *N. Tr.* 22, 2, 254.

GUÉRIN-VARRY. *Ann. Chim. Phys.* 49, 248; *Schw.* 65, 220; *N. Tr.* 26, 2, 155; abstr. *Pogg.* 29, 50; *Berz. Jahresb.* 13, 276. — *Ann. Chim. Phys.* 51, 222.

BIOT & PERSOZ. *Ann. Chim. Phys.* 52, 85; *Pogg.* 32, 160; *Schw.* 68, 163; abstr. *Ann. Pharm.* 6, 210.

GUIBOURT. *J. chim. méd.* 8, 419; *Ann. Pharm.* 9, 221.

MULDER. *Bull. de Néerlande*, 1838, 167; abstr. *J. pr. Chem.* 16, 244.

- HERBERGER. *Repert.* 47, 19; *Pharm. Centr.* 1834, 193.  
 LASSAIGNE. *J. chim. méd.* 18, 416 and 821; abstr. *Berz. Jahresb.* 23, 381.  
 BUCHNER. *Ann. Pharm.* 45, 89.  
 SCHMIDT. *Ann. Pharm.* 51, 29.  
 NEUBAUER. *J. pr. Chem.* 62, 193; abstr. *Pharm. Centr.* 1854, 637. —  
*Ann. Pharm.* 102, 105; abstr. *J. pr. Chem.* 71, 255; *Chem. Centr.*  
 1857, 590.  
 LUDWIG. *N. Br. Arch.* 82, 33, and 153; abstr. *Chem. Centr.* 1855, 376.  
 A. GÉLIS. *Compt. rend.* 44, 144; *N. J. Pharm.* 31, 216; *J. pr. Chem.*  
 71, 378; abstr. *N. Br. Arch.* 96, 192.  
 HEKMEIJER. *Scheik. Verhandl. en Onderzoek.* 2, 2, 167; abstr. *Kopp's*  
*Jahresber.* 1858, 482.  
 E. FREMY. *Compt. rend.* 50, 124; *N. J. Pharm.* 37, 81; abstr. *Chem.*  
*Centr.* 1860, 607.  
*Vegetable gum. Pflanzengummi. Gomme, Muqueux. Gummie acid (Fremy).*  
*Arabin (Neubauer).*

*Sources.*—In the vegetable and animal kingdoms, in the former universally diffused, as contents of the cells, or as secretion in the gum-ducts, from which, as they burst, the gum exudes and slowly dries and hardens on the bark. It forms the gum-arabic or gum-senegal of commerce, which exudes from various species of acacia growing in Arabia, Egypt, and other countries.

The following plants contain gum which, however, is only partially identical with gum-arabic. The roots of *Anacyclus Pyrethrum* (*Phytochem.* 66);\* *Bryonia alba* (Schwerdfeger, *Jahrb. pr. Pharm.* 7, 287); *Cephalis Ipecacuanha* (Willigk, *Wien. Akad. Ber.* 5, 190); *Rumex acutus* (Bley, *N. Tr.* 25, 2, 68); *Typha angustifolia*, especially in spring (Lecocq, *J. Pharm.* 14, 221); *Valeriana officinalis* (Trommsdorff, *N. Tr.* 18, 1, 3); the bulbs of *Colchicum autumnale* (Pelletier & Caventou, *Ann. Chim. Phys.* 14, 69). The root-stocks of *Asplenium filix fœmina* (Bock, *N. Br. Arch.* 65, 257); *Polypodium vulgare* (Desfosses, *J. Pharm.* 14, 246); *Veratrum album* (Pelletier & Caventou, *Ann. Chim. Phys.* 14, 69).—In the herb of *Calluna vulgaris* (Bley, *Repert.* 15, 329); the bark of various species of *Cinchona* (Reichardt, Reichel, *Phytochem.* 50); in *Cinchona nova* (Pelletier & Caventou, Winckler; Hlasiwetz, *Ann. Pharm.* 79, 142); *Croton Eluteria* (Duval, *Phytochem.* 23); *Salix alba* (Pelletier & Caventou, *J. Pharm.* 7, 123; *Repert.* 12, 213); *Sambucus nigra* (Krämer, *N. Br. Arch.* 43, 20); *Swietenia febrifuga* (Overbeck, *N. Br. Arch.* 68, 271).—The leaves of *Ampelopsis hederacea* (Wittstein, *Repert.* 46, 317); *Calendula officinalis* (Geiger, *Diss. de Calend. off.* Heidelberg, 1818); *Taxus baccata* (Peretti, *J. Pharm.* 14, 537). The leaf-buds of *Populus nigra* (Pellerin, *J. Pharm.* 8, 425; *N. Tr.* 7, 1, 390).—The flowers of *Calendula officinalis* (Geiger, *loc. cit.*); *Tilia*? (Marggraf, *Pfaff Mat. med.* 4, 92); *Tropæolum majus* (Müller, *Ann. Pharm.* 25, 207); the honey-dew of *Tilia parvifolia*, in smaller quantity than of *T. grandiflora* (Riegel, *Jahrb. pr. Pharm.* 14, 155); *Crocus* (saffron) (Aschoff, *Berl. Jahrb.* 1818, 142).—The fruit of *Areca Catechu* (Morin, *J. Pharm.* 81, 449); *Musa paradisiaca* (Boussingault, *Phytochem.* 84); *Anassia sativa* (Adet, *Scher. J.* 1, 663); *Pyrus malus*

\* This and the corresponding references in the following pages, are to Rochleder's "Phytochemie" in the German edition of *Gmelin's Handbuch*, vol. viii.



(Bérard, *Phytochem.* 17); *Rubus fruticosus* (Lupp, *Ann. Pharm.* 101, 219); the unripe fruit of *Citrus Aurantium* (Lebreton, *J. Pharm.* 14, 377); the ripe berries of *Lonicera Xylosteum* (Enz, *Pharm. Viertelj.* 5, 196); *Juniperus communis* (Witting, *N. Br. Arch.* 91, 296); *Vitis vinifera* (Proust, *N. Gehl.* 2, 93; Bérard).—The seed of *Amomum Grana Paradisi* (Sandrock, *N. Br. Arch.* 73, 18); *Croton Tiglium* (Pelletier & Caventou, *Phytochem.* 23); *Hura crepitans* (Bonastre, *J. Pharm.* 10, 479); *Ignatia amara* (Pelletier & Caventou, *Ann. Chim. Phys.* 10, 147); *Ricinus communis* (Geiger, *N. Tr.* 2, 2, 173); *Piper nigrum* (Pelletier, *Ann. Chim. Phys.* 16, 337); rice (Braconnot, *Ann. Chim. Phys.* 4, 76); the seed of *Schoenocaulon officinale* (Pelletier & Caventou, *Ann. Chim. Phys.* 14, 69); maize (Stepf, *J. pr. Chem.* 76, 88).

Gum forms part of the exuded and hardened juice of the stems of acacia, apricot, cherry, almond, peach, and plum trees, of the juice of the lime tree (Riegel); of the juice of mangold-wurzel (Kircher, *Ann. Pharm.* 31, 337); of the juice of *Rosa rubrifolia* (Addams, *Phytochem.* 16); of the milky juice of *Ficus elastica* (Nees v. Esenbeck & Marquart, *Ann. Pharm.* 14, 42); *Galactodendron utile* (Solly, *Phytochem.* 75); *Platanus occidentalis* (John, *Chem. Schrift.* 4, 7); *Lactuca virosa* (Pfaff & Link, *Mat. méd.* 6, 501); hence it is also found in swollen and hardened milky juice, the gum-resins of commerce, together with resin, as in lactucarium (Walz, *Ann. Pharm.* 32, 85), asafoetida (Hlasiwetz, *Ann. Pharm.* 71, 23), myrrh, incense, sandarach, &c. Olibanum, also a gum-resin, contains a gum agreeing in properties with arabin. (Hekmeljer).—It occurs in gall-nuts (Guibourt, *Ann. Pharm.* 48, 359); in the manna of *Eucalyptus dumosa* (Anderson, *N. Ed. Phil. J.* 47, 132; *J. pr. Chem.* 47, 449); in trehala. (Guibourt, *Compt. rend.* 46, 1213).

*Ulcularia esculenta* (Kirchhoff, *Phytochem.* 95), *Lecanora Parellula* (Schunck, *Ann. Pharm.* 54, 257), and *Parmelia parietina* (Herberger, *Repert.* 47, 179) contain gum.

*Enumeration of Gums, whose preparation and behaviour with various re-agents are described in the following places:* 1. Gum-acajou, the dried juice of *Anacardium occidentale* (Trommsdorff, *N. Tr.* 22, 2, 254; Ludwig, *N. Br. Arch.* 82, 33).—2. Gum Ammoniacum (Braconnot, *Ann. Chim.* 68, 73).—3. From Valerian stalks (Braconnot, *Ann. Chim.* 70, 238).—4. Gum-bdellium (Pelletier, *Schw.* 5, 248).—5. From the seeds of the Baobab tree, *Adansonia digitata* (Vauquelin, *Schw.* 35, 45).—6. From Catechu (Pfaff *Syst. d. Mat. méd.* 2, 189).—7. Gum-embavi (Ludwig, *N. Br. Arch.* 82, 33; Gruner, *Pharm. Centr.* 1851, 352).—8. From Gentian roots, *Gentiana lutea* (Braconnot, *J. Phys.* 84, 346).—9. From Geoffroya bark (Hüttenschmid, *Phytochem.* 8).—10. From Stag's morel (Biltz, *N. Tr.* 11, 2, 3).—11. From the bulb and leaves of the hyacinth (Bostock, *N. Gehl.* 8, 573; Leroux, *Scher. J.* 7, 212; John, *Chem. Schrift.* 6, 14).—12. From Maize (Stepf, *J. pr. Chem.* 76, 92).—13. From Mistletoe-berries (Henry, *Phytochem.* 47).—14. From Myrrh (Pelletier, *Schw.* 5, 254; Braconnot, *Ann. Chim.* 68, 55; Hekmeljer *Scheik. Verhandl.* 22, 167).—15. Gum-opoponax (Pelletier, *Schw.* 5, 259).—16. Persian gum (Martius, *Ann. Pharm.* 21, 63).—17. From Spanish pepper (Braconnot).—18. From Rosewood (Guibourt, *Ann. Pharm.* 9, 227).—19. From Saponaria-root (Schrader, *Schw.* 9, 139; Braconnot, *J. Phys.* 84, 289).—20. From Senna-leaves (Braconnot, *J. Phys.* 84, 281).—21. From the tubers of Sun-flowers (*Phytochem.* 67).—22. From Tea-leaves (Mulder, *Pogg.* 43, 638).—23. From Centaury (Schrader, *Schw.* 9, 143).—24. From Juniper-berries (Trommsdorff, *Phytochem.* 79).—24. From Frankincense (Braconnot, *Ann. Chim.* 68, 63; Hekmeljer, *Scheik. Verhandl.* 2, 2, 167).—25. From Bryony (*Phytochem.* 37; Brandes & Firnhaber, *N. Br. Arch.* 3, 351).

A few of the somewhat better known gums are added as an Appendix.

*In the Animal Kingdom.*—Cockchafers, silk-worms, and the liver and

gills of the craw-fish contain a gum agreeing in its properties with arabin. (Städeler, *Ann. Pharm.* 111, 26.)

*Formation. From the isomeric body, Metagummic acid.*—1. By bringing this substance in contact with aqueous alkalis or alkaline earths. (Neubauer, Fremy).—2. By boiling metagummate of lime with water (Gélis); hence also the insoluble part of cherry tree gum is rendered soluble by prolonged boiling with water (Guérin-Varry), more quickly with aqueous alkaline carbonates. (Fremy.) On the formation of gum by the lactic acid fermentation of cane-sugar, according to Bensch's process (xi, 475), see *Cane-sugar*; on the formation of gum by the decomposition of tannic acid, see that substance. — Hofmann obtained a gum agreeing with gum-arabic, by the spontaneous decomposition of pyroxilin (p. 175). Gum is formed by the continued boiling of seaweed mucilage with dilute sulphuric acid. (*Ed. Phil. J.* 26, 409.)

*Preparation. From Gum-arabic.* A solution of gum prepared with cold water and as concentrated as possible is mixed with sufficient hydrochloric acid to produce a strong acid re-action, and precipitated with alcohol; the precipitate is washed with alcohol, dissolved in water containing hydrochloric acid, and again precipitated with alcohol; and the resulting precipitate is washed with alcohol till all the hydrochloric acid is removed. (Neubauer). — ¶. A strong solution of gum, mixed with 4 or 5 p. c. of hydrochloric acid, is subjected to dialysis until it no longer gives a precipitate with nitrate of silver. — In operating with a 20 p. c. solution of gum, the proportion of ash can be reduced in this way to 0.1 p. c. in 5 days. — (Graham, *Phil. Trans.* 1861, p. 214, *Chem. Soc. J.* 15, 257; *Ann. Pharm.* 121, 53.) ¶.

*Properties.* In the moist state, a milk-white amorphous mass, which becomes glassy and transparent when dry. Reddens litmus. (Neubauer). Its power to redden litmus is comparable to that of carbonic acid; 100 pts. arabic acid is neutralised by 2.85 pts. potash. (Graham.) Gum-arabic possesses lævo-rotatory power (Biot & Persoz); for pure gum (?),  $[\alpha] = 36^\circ$  to the left. (Béchamp, *Compt. rend.* 51, 256.) On the colours and figures of gum-arabic in polarised light, see Roussin (*N. J. Pharm.* 37, 411). — Diffusive power, half as great as that of tannic acid, 400 times less than that of chloride of sodium. (Graham.)

	at 100°.		Neubauer. mean.
24 C.....	144 .....	42.12 .....	41.97
22 H .....	22 .....	6.41 .....	6.51
22 O .....	176 .....	51.47 .....	51.52
$C^{24}H^{22}O^{22}$ .....	312 .....	100.00 .....	100.00

*Gum-arabic or Gum-senegal.*

	Berzelius.	Prout.	Göbel.	Gay-Lussac & Thénard.	Berthollet.	Saussure.
C	42.68 .....	41.4 .....	42.2 .....	42.23 .....	43.90 .....	45.84
H	6.37 .....	6.5 .....	6.6 .....	6.93 .....	6.86 .....	5.46
O	50.95 .....	52.1 .....	51.2 .....	50.84 .....	49.24 .....	48.70
	100.00 .....	100.0 .....	100.0 .....	100.00 .....	100.00 .....	100.00

	Guérin-Varry.			Mulder.		
	a.	b.		a.	b.	c.
C.....	43·81	43·59	.....	44·6	44·40	44·70
H .....	6·20	6·23	.....	6·1	6·09	6·09
O .....	49·99	50·18	.....	49·3	49·51	49·21
	100·00	100·00	.....	100·0	100·00	100·00

The analyses of the gums, with the exception of Mulder's, were calculated according to the old atomic weight of carbon. — Guérin-Varry analysed gums dried at 125°, *a.* gum-arabic, *b.* gum-senegal. Mulder, gums dried at 130°; *a.* gum-arabic, *b.* gum-senegal, *c.* Java gum. The other analyses relate to the substance dried at 100°.

The earlier formulæ were deduced from the analyses of gum-arabic; for air-dried gum,  $C^4H^5O^4$  (Ure); gum dried at 100°,  $C^{17}H^{16}O^{16}$  (Prout),  $C^{12}H^{11}O^{11}$  (Berzelius, Liebig), gum dried at 125°,  $C^{12}H^{10}O^{10}$  (Guérin-Varry, Mulder). Gum-arabic dried at 100° gives off 1 at. water at 120°, and is then  $C^{12}H^{10}O^{10}$  (Gélis). — On the specific gravity of gum-arabic, and the amount of ash which it yields, see *Arabate of Lime*.

*Decompositions.* 1. Arabic acid, which in the moist state dissolves readily in water, becomes insoluble after drying at mean temperature, or at 100°, and, when water is poured upon it, swells up to a jelly, like frog-spawn. (Neubauer, Graham.) Doubtless in consequence of the formation of metagummic acid (Kr.). Gum-arabic dried at 120° becomes insoluble, but without loss of water when heated for some time to 150° (Gélis), being converted into metagummate of lime (Fremy). Gum-arabic roasted with oxalic acid yields oxalate of lime and metagummic acid (Fremy). Arabic acid heated for some time to 170°, gives off 3·17 p. c. of its weight and turns yellowish brown (Neubauer).

Gum-arabic turns yellow between 135° and 140°, becomes darker as the temperature rises, gives off, between 166° and 180°, the empyreumatic odour of burnt sugar, then assumes a brown colour, and becomes partially insoluble in water (Mulder). After drying at 100°, it loses 2·6 p. c. of its weight when heated to 150° — 177°, and turns brown (Prout), at the same time producing an acid. (Vaudin, *J. Pharm.* 9, 193.)

Gum-arabic yields by *dry distillation* a gaseous mixture, consisting of carbonic acid, hydrogen, carbonic oxide and hydrocarbons, a distillate of empyreumatic acetic acid, and a residue of charcoal mixed with carbonate of lime, and a little phosphate (Cruikshank). 100 pts. gum yield 53·9 pts. of a thick brown distillate less acid than that obtained from sugar, and leave 28·6 pts. of charcoal and ash. (Vauquelin, *Bull. Pharm.* 3, 49.)

2. When *dry air* at 14° is passed over gum-arabic, a large quantity of carbonic acid is formed. (Karsten, *Berl. Akad. Ber.* Jan. 1860; *J. pr. Chem.* 79. 226.)

3. The aqueous solution of gum turns acid on *standing* (only when air has access to it, according to Guérin-Varry), and after a very long time produces a peculiar sugar, which turns the plane of polarisation of a luminous ray to the right,  $\frac{1}{3}$  less than grape-sugar, and does not form mucic acid with nitric acid (Fermond, *Berthelot Chim. org.* 2, 250). According to Maumené (*Compt. rend.* 39, 914; *J. pr. Chem.* 64, 147) it does not change either at ordinary or at higher temperatures, and preserves its rotatory power unaltered for months.

4. When *oil of vitriol* is covered with a layer of very strong solution of gum, the gum, after standing for some hours, is completely con-

verted into metagummic acid. (Fremy.) Gum-arabic previously freed from lime by oxalic acid is not converted into metagummic acid under these circumstances (Fremy).—When pulverised gum-arabic is triturated with oil of vitriol, it becomes coloured, after some hours; and on diluting with water, neutralising with chalk, then filtering the solution, and evaporating, sulphogummic acid remains, together with a peculiar gum resembling that which is produced from linen by the action of sulphuric acid (Braconnot), and not capable of fermenting with yeast (Guérin-Varry). Gum heated with oil of vitriol, becomes carbonised, and forms water together with traces of acetic acid (Proust, *A. Gell.* 3, 43), artificial tannin (Hatchett), and malic acid (Link).

The aqueous solution of gum-arabic, when left to stand for some time in contact with dilute sulphuric acid; loses its lævo-rotatory power—more quickly when heated or boiled with the acid—and, if the temperature be gradually raised to 96°, quickly acquires dextro-rotatory power, which remains unaltered after prolonged boiling. At the moment when the rotatory power changes from left to right, the solution contains gum-dextrin, precipitable by alcohol, resembling gum-arabic when dry, yielding mucic acid with nitric acid; but after boiling for some time, it is no longer precipitable by alcohol, and then contains a fermentable sugar (Biot & Persoz); probably identical with galactose, the product obtained from milk-sugar by the action of acids. (Berthelot, *Chim. org.* 2, 219.)

The acid mixture of gum-mucilage and dilute sulphuric acid, if left to cool before it ceases to be precipitable by alcohol, deposits flocks containing gum-dextrin mixed with gypsum. If the former be removed by washing with acidulated water, and the latter by boiling with dilute soda-solution and subsequent washing with acidulated water, the flocks dissolve at the moment when all the acid is removed, forming an optically inactive mucilage. (Biot & Persoz, *Ann. Chim. Phys.* 2, 249.)

5. When gum-arabic is heated with water, bicarbonate of potash, and iodine, iodoform is produced. (Millon, *Compt. rend.* 21, 828; *J. pr. Chem.* 37, 53.) Iodine does not colour gum-arabic (Ludwig); aqueous *iodic acid* decomposes it at the boiling heat.

6. Powdered gum absorbs *chlorine gas*, with evolution of carbonic acid, turning brown and deliquescing to a compound of decomposed gum, with hydrochloric acid. (Bouillon-Lagrange & Vogel.)—Gum re-acts with chlorine, either moist or dry, exactly like starch (p. 83), (Liebig). Chlorine gas passed through the aqueous solution, appears to form citric acid (Vauquelin). Guérin-Varry and Simonin were not able to find this acid.—When chlorine gas is passed for some time through a dilute solution of gum, the liquid, after standing for some time, deposits white flocks, which have an acid re-action, even after washing, smell like chlorine, and contain chlorine, nitrogen, and gum (Guérin-Varry). When a gum-solution saturated by the prolonged passage of chlorine is neutralised with chalk, and the filtrate evaporated to a syrup is mixed with alcohol, a pasty lime-salt soluble in water is precipitated, whereas on supersaturating with hydrate of lime, an insoluble lime-salt is obtained. The latter, decomposed with sulphuric acid, yields a peculiar, non-crystallisable acid, whose solution is precipitated by neutral acetate of lead, but not by nitrate of silver. (Simonin, *Ann. Chim. Phys.* 50, 319.)

7. Powdered gum absorbs *hydrochloric acid* gas and deliquesces to a soft brown mass, from which sulphuric acid eliminates hydrochloric acid. (Bouillon-Lagrange & Vogel.) Fuming hydrochloric acid dissolves gum with brown colour, and separates carbonic acid on cooling. The solution, after being neutralised with ammonia, leaves on evaporation a residue which is soluble in alcohol, melts when heated, and smells like burnt sugar. (Fourcroy.)

8. Gum immersed in *fuming nitric acid* is converted into xyloidin (Braconnot), nitro-gum (Béchamp); when immersed in *nitrosulphuric acid*, it is converted into an explosive substance resembling pyroxylin (Flores-Domonte & Ménard, Svanberg); into binitro-gum (Béchamp.) — Gum heated with moderately concentrated nitric acid, is decomposed, with formation of mucic acid (Fourcroy & Vauquelin), saccharic acid (Guérin-Varry), oxalic and tartaric acids. (Liebig, *Ann. Pharm.* 113, 4.)

a. When 1 pt. gum is triturated in a cooled mortar with 3 pts. fuming nitric acid, and after complete solution, the still gummy liquid is diluted with 20–30 pts. water, a precipitate is formed consisting of dextro-rotatory nitro-gum  $C^{12}H^8O^9, NO^5$ , which, after washing and drying, cakes together into a horny mass, and dissolves in alcohol of 90 p. c., whence it is obtained as a white mass which becomes electric by friction. (Béchamp.) — When a solution of 1 pt. gum in 5 pts. fuming nitric acid is precipitated by 3 pts. oil of vitriol, and the cake is comminuted and suspended in 20–30 vols. water, a hard precipitate is obtained which remains pulverulent after drying, and yields to alcohol 95 p. c. of dextro-rotatory binitro-gum,  $C^{12}H^8O^8, 2NO^4$ , whilst another compound remains dissolved. (Béchamp, *Compt. rend.* 51, 256. — See also Flores-Domonte & Ménard, *Compt. rend.* 24, 89; *N. J. Pharm.* 12, 159; — Svanberg, *Berzel. Jahresber.* 27, 394; — Reinsch, *Jahrb. pr. Pharm.* 481, 102.)

b. Gum-arabic heated with an equal weight of nitric acid of sp. gr. 1.34 is but partially decomposed; with two parts of the acid, it is decomposed, with formation of saccharic acid; heated with 4 pts. nitric acid, it yields 16.88 p. c. mucic acid and a small quantity of oxalic acid; with 6 pts. or more of nitric acid, a smaller quantity of mucic but a larger quantity of oxalic acid is obtained. (Guérin-Varry.) Respecting the formation of tartaric acid, see *Milk-sugar*. The saccharic acid produced at the same time (xi. 513) was formerly mistaken for malic acid. — Gum-arabic, which is lævo-rotatory, becomes dextro-rotatory under the influence of nitric acid (and indeed by the action of dilute acids in general), this power, however, becoming weaker as the oxidising action of the nitric acid, and the formation of mucic acid begin and advance. The liquid now acquires lævo-rotatory power equal to that which the gum-arabic originally possessed, then exhibits indications of the presence of oxalic acid, and again loses part of its lævo-rotatory power, without however becoming quite inactive, inasmuch as a lævo-rotatory substance remains dissolved in the mother liquors. Hence the mucic acid appears to be formed from a dextro-rotatory, the oxalic acid from a lævo-rotatory substance contained in the gum. (Dubrunfaut, *Compt. rend.* 42, 232.)

9. Gum heated in sealed tubes with bromine, yields a colourless or yellowish liquid, probably  $C^{12}H^{10}O^{10}Br^2$ , which, when treated with oxide of silver, oxide of lead, or caustic soda, is converted into *isobiglycoethylenic acid*  $C^{12}H^{10}O^{12}$ . (Barth & Hlasiwetz: see p. 232.)

10. By gaseous *fluoride of boron* gum is slowly liquefied, without blackening. (Berthelot, *N. Ann. Chim. Phys.* 38, 38.)—11. Gum on which warm *aqueous arsenious acid* is poured, turns brown, perhaps with formation of sugar. (Baumann, *N. Br. Arch.* 37, 50.)—12. Heated for some time with aqueous *osmic acid*, it yields oxalic acid, probably also acetic acid, and a substance precipitable by basic acetate of lead. (Buttlerow, *J. pr. Chem.* 56, 276.)

13. Gum heated to 150° with aqueous *ammonia*, is converted into a brown nitrogenous mass, resembling that which is produced under similar circumstances, from starch (p. 87). (Schützenberger.)—14. Heated with 4—5 pts. *hydrate of potash* and a small quantity of water, it is decomposed, with formation of oxalate of potash (Gay-Lussac), also of carbonate, formiate, acetate, and propionate of potash, with the same appearances as are observed in the corresponding decomposition of starch or of cane-sugar (Gottlieb; see vii. 135; xv. 88; also *Cane-sugar*).—15. By the dry distillation of powdered gum with 8 pts. *quicklime*, an oily distillate is produced containing acetone (ix. 1.) and a small quantity of metacetic. (Fremy, *Ann. Chim. Phys.* 59, 6.)

16. Aqueous gum-solution mixed with a small quantity of *nitrate of silver*, reddens immediately in sunshine, gradually in diffused daylight, and gradually deposits metallic silver. (Rouchas, *J. Pharm.* 17, 116; *N. Tr.* 24, 2, 187.)—17. Aqueous *ferricyanide of potassium*, in presence of free alkali, oxidises gum to carbonic acid and water, but less quickly than cane-sugar. (Wallace, *Chem. Soc. Qu. J.* 7, 77; *J. pr. Chem.* 64, 77.)

18. Gum-solution does not ferment in contact with yeast (Cruikshank), it is not altered by the saliva or the gastric juice. (Frerichs; Blondlot, *Handb. Zoochemie*, viii, 577.) Gum left in contact with *cheese* and *chalk* in a warm place, yields alcohol and a small quantity of lactic acid, without previous formation of yeast, but neither mannite nor glycerin. (Berthelot, *N. Ann. Chim. Phys.* 50, 365.)

*Combinations. With Water.*—Air-dried gum-arabic contains water, which escapes in vacuo, or when the gum is heated. For further details, see *Arabate of Lime* (p. 201).

Moist arabic acid dissolves readily in water, forming a solution which is not precipitated by alcohol unless the arabic acid contains mineral acids or salts. A drop of nitric acid, hydrochloric acid, or solution of common salt added to the solution mixed with alcohol, produces complete precipitation. (Neubauer). Similar appearances are presented by the mucilage of *Gummi arabicum electum*, when it is mixed with twice its volume of alcohol of 76 vol. p. c. A drop of hydrochloric acid or solution of common salt produces coagulation; a larger quantity of either liquid dissolves the whole. With other sorts of gum-arabic, alcohol likewise produces coagulation which disappears on addition of hydrochloric acid. (Ludwig, *N. Br. Arch.* 82, 155). According to other statements, gum-mucilage is precipitated by alcohol, even if it contains only  $\frac{1}{10}$  p. c. of gum. (See also *Preparation of arabic acid*, p. 197.)

The aqueous solution of gum-arabic or gum-senegal is called *Mucilage* (*Mucilago*, *Gummischleim*). It is more or less viscid, glutinous, transparent or translucent, colourless to pale yellowish brown. 100 pts. of water at 15° dissolve 100 pts. of gum-arabic; at 100°, from 108 to 116 pts. (Herberger); of gum-senegal, 100 pts. water dissolve 72 pts. at 15°, and 96 pts. at 100° (Herberger): according to Guérin-Varry,

18.5 pts. at  $20^{\circ}$ , and 24.14 pts. at  $100^{\circ}$ .—Mucilage is thickened by borates, not by free boracic acid, or free alkali; acids restore the fluidity (Schiller, *Berl. Jahrb.* 1808, 186; Buchholz, *Taschenb.* 1811, 288; Lambert & Gresecke, *Schur.* 43, 491; Vogel, *Br. Arch.* 17, 50; Herberger; Ludwig), Mucilage is precipitated by sulphate of soda (Barreswil, *N. J. Pharm.* 17, 124); clouded and precipitated in white flocks by silica-solution. (Thomson, Herberger), not, according to Guérin-Varry.—Aqueous ferric sulphate causes mucilage to coagulate to a jelly (Bracconnot), an effect likewise produced by ferric chloride. Gum-solution mixed with a small quantity of a ferric salt is not precipitated by alkalis. (Rose.)

*With Bases.* Arabic acid unites with alkalis and alkaline earths, forming arabates, which are precipitated from their aqueous solutions by alcohol. It decomposes alkaline carbonates, and expels the carbonic acid. (Neubauer.)

*Arabate of Potash.* Precipitated by alcohol from the solution of arabin in potash-ley free from carbonic acid. (Neubauer.)

at $100^{\circ}$ .				Neubauer.	
36 C	.....	216.0	....	40.52	.... 40.24
30 H	.....	30.0	....	5.63	.... 5.72
30 O	.....	240.0	....	45.03	.... 44.80
KO	.....	47.2	....	8.82	.... 9.24
<hr/>					
$3C^{12}H^{10}O^{10}, KO$	.....	533.2	....	100.00	.... 100.00

So according to Neubauer.

Submitted to dialysis, it loses potash, arabic acid remaining with an acid re-action. (Graham.)

*Arabate of Baryta.*—From the solution of arabic acid in excess of baryta-water, alcohol throws down a precipitate containing 17.62 p. c. baryta. If excess of arabic acid is present, the precipitate contains from 10.93 to 11.15 p. c. baryta, and dissolves in water forming a gummy liquid. (Neubauer.)

at $100^{\circ}$ .				Neubauer.	
24 C	.....	144.0	....	36	.... 36.63
20 H	.....	20.0	....	5	.... 5.16
20 O	.....	160.0	....	40	.... 40.59
BaO	.....	76.5	....	19	.... 17.62
<hr/>					
$2C^{12}H^{10}O^{10}, BaO$	.....	400.5	....	100	.... 100.00

*Arabate of Lime.*—Gum arabic forms with lime a compound which is decomposed by the carbonic acid of the air (Kuhlmann, *Ann. Pharm.* 27, 22) and deposits pentahydrated carbonate of lime. (Pelouze, *Ann. Chim. Phys.* 48, 307.) The solution exposed to the current of the voltaic battery deposits hydrated carbonate of lime with the same appearances as a solution of lime in sugar. (Becquerel, *Ann. Chim. Phys.* 47, 12.)  
*a.* When aqueous arabic acid is mixed with excess of an ammonical solution of chloride of calcium, and alcohol added, a precipitate is obtained, which after drying at  $100^{\circ}$ , has the composition  $C^{12}H^{10}O^{10}, CaO + 2C^{12}H^{10}O^{11}$  (Hekmeljer).—*b.* When arabic acid is boiled with water and excess of milk of lime, alcohol throws down from the strongly alkaline filtrate, a gummy precipitate which contains 8.51 p. c. lime and absorbs carbonic acid from the air. (Neubauer).—*c.* By dis-

solving arabic acid in lime-water and precipitating with alcohol, a precipitate is formed which contains 2.95 p. c. lime, and dissolves in water, forming an alkaline mucilage. If a smaller quantity of lime-water be used, the precipitate contains from 2.14 to 2.55 p. c. lime, and has an acid or neutral re-action.

<i>According to b.</i>				Neubauer. at 100°.
24 C.....	144	....	40.90	.... 40.45
20 H.....	20	....	5.68	.... 5.70
20 O.....	160	....	45.47	.... 45.34
CaO .....	28	....	7.95	.... 8.51
<hr/>				
2 C <sup>12</sup> H <sup>10</sup> O <sup>10</sup> , CaO .....	352	....	100.00	.... 100.00
<hr/>				
<i>According to c.</i>				Neubauer. at 100°.
72 C .....	432	....	43.2	.... 43.07
60 H .....	60	....	6.0	.... 6.35
60 O .....	480	....	48.0	.... 47.63
CaO .....	28	....	2.8	.... 2.95
<hr/>				
6 C <sup>12</sup> H <sup>10</sup> O <sup>10</sup> , CaO .....	1000	....	100.0	.... 100.00

The gum-arabic and gum-senegal of commerce consist essentially of arabate of lime mixed with arabate of potash; hence when burnt, they leave about 3 per cent. of ash consisting for the most part of carbonate of potash and carbonate of lime. — Sp. gr. of gum-arabic = 1.355 (Guérin-Varry), 1.49 (Herberger); of gum-senegal, 1.43 (Guérin-Varry), 1.62 (Herberger). Reddens litmus. In the air-dried state, it contains from 12.4 to 17 p. c. hygroscopic water which escapes when the gum is heated (see also Gélis, p.198. On the composition of the ash of gum-arabic, see Löwenthal & Hausmann, *Ann. Pharm.* 89, 112). Alcohol extracts from gum-arabic or gum-senegal, 0.4 — 0.5 p. c. glucose. (Ludwig *N. Br. Arch.* 82, 39.)

*Arabate of Lead.*—Basic acetate of lead added to aqueous arabin throws down a white precipitate which contains 30.64 p. c. oxide of lead, turns yellow at 100°, brown between 160° and 180°, and after prolonged washing, still retains 27 p. c. oxide of lead. (Neubauer.)

<i>at 100°.</i>				Neubauer.
36 C.....	216.0	....	30.46	.... 30.88
30 H.....	30.0	....	4.23	.... 4.33
30 O.....	240.0	....	33.85	.... 34.15
2 PbO .....	223.4	....	31.46	.... 30.64
<hr/>				
3 C <sup>12</sup> H <sup>10</sup> O <sup>10</sup> , 2PbO .....	709.4	....	100.00	.... 100.00

Gum-mucilage dissolves oxide of lead (Peschier, *J. Pharm.* 3, 509), forming a heavy, coherent compound (Berzelius). Gum-mucilage is not precipitated by neutral acetate or nitrate of lead, but the basic acetate or basic nitrate produces a copious white precipitate [the basic acetate even in very dilute solutions (Städeler, *Ann. Pharm.* 111, 26)]. *a.* When the mucilage is mixed with basic acetate or nitrate of lead, or when nitrate of lead is added to slightly ammoniacal mucilage



till the alkaline re-action disappears, but not till the whole of the gum is precipitated; the curdy precipitate, which is very friable when dry, contains 38.25 p. c. oxide of lead (Berzelius, *Lehrb.* 3 Aufl. 6, 400) from 37.9 to 38.1 p. c. (Riegel, *N. Br. Arch.* 55, 155). When mucilage is dropped into an excess of basic acetate of lead, the precipitate, after drying at  $130^{\circ}$ , contains 37.27 p. c. oxide of lead, but when the basic acetate is added to excess of mucilage, the precipitate contains 30.15 p. c. (Mulder.)

*Arabate of Copper.*—From an aqueous solution of arabin mixed with acetate of copper, alcohol throws down a precipitate of the formula  $C^{10}H^{10}O^{10}$ ,  $CuO + C^{12}H^{11}O^{11}$  (Hekmeljer).—When aqueous gum-arabic is mixed with potash-ley, and then with sulphate of copper, a blue precipitate is formed, which is insoluble in pure water, and does not blacken even at the boiling heat. (Trommer, *Ann. Pharm.* 39, 360.)

The sky-blue precipitate is permanent in the air, turns brown after immersion for some time in boiling water, and after drying in vacuo, contains 40.2 p. c. cupric oxide. (Lassaigue, *J. chim. méd.* 182, 416.) When gum-mucilage is mixed with a small quantity of sulphate of copper, then with excess of potash-ley, and slightly warmed, an azure-coloured solution is formed, which remains clear and blue when boiled. If the gum contains sugar (which can be extracted by alcohol), the protoxide of copper is reduced to dioxide (Ludwig, *N. Br. Arch.* 82, 157).—When gum-mucilage is boiled for a long time with aqueous cupric acetate, a brown precipitate separates, and the filtrate after standing for a while deposits red cuprous oxide. (Peschier, *J. Pharm.* 3, 509).—Gum dissolves in aqueous cuprammonia (Cramer, *J. pr. Chem.* 73, 15), and when added to a solution of cellulose in that liquid precipitates the cellulose completely. (Schlossberger, *Ann. Pharm.* 107, 24.)

Gum-solution dissolves *mercurous* and *mercuric oxide*. (Peschier, *J. Pharm.* 3, 509.) It forms a white precipitate with mercurous nitrate, but does not precipitate mercuric salts or *terchloride of gold* (Pfaff). It is not precipitated by *infusion of galls* (Pfaff).—Concentrated gum-mucilage is not precipitated either by *indigo* or by *carmine*. Maschke, *J. pr. Chem.* 76, 47.)

Arabic acid and gum-arabic are insoluble in *alcohol* and in *ether*. Alcohol frees gum-arabic from foreign substances. — *Glycerin* dissolves gum-arabic (Cap & Garot, *N. J. Pharm.* 26, 81).

¶ *With Gelatin.*—On mixing solutions of arabic acid and gelatin, oily drops are precipitated which solidify to a nearly colourless jelly by standing. This compound melts at  $25^{\circ}$ . It may be washed with water without decomposition, but is slightly soluble in warm water, more so in solution of gelatin. The oily drops and the jelly contain 83.5 p. c. water. Prepared with excess of arabic acid, and dried at  $100^{\circ}$ , it contained 100 pts. arabic acid to 59 pts. gelatin. Solution of gelatin is not precipitated by solution of unpurified gum, or by solution of arabate of potash. (Graham, *Phil. Trans.* 1861, p. 215; *Chem. Soc. Qu. J.* 15, 258; *Ann. Pharm.* 121, 57). ¶

*Appendix to Arabic Acid and Gum.*

1. *Gum from Gamboge.*—When gamboge is exhausted with ether and absolute alcohol, the residue boiled with water, concentrated and precipitated by water, a gummy precipitate is obtained, which may be freed from colouring matter by washing with alcohol. — After drying at  $110^{\circ}$  and trituration, it forms a pale yellow powder, containing 44.47 p. c. C., 6.16 H., and 49.37 O., therefore  $C^{12}H^{10}O^{10}$ . — With nitric acid, it yields mucic acid, and with dilute sulphuric acid, after 12 hours' boiling, a red-brown, very sweet, non-fermentable sugar. (Buchner, *Ann. Pharm.* 45, 89.)

2. *Gum from Ipecacuanha root.*—The decoction of the root is freed from phosphoric acid by precipitation with neutral acetate of lead; the filtrate is precipitated with basic acetate of lead, the washed precipitate is suspended in water and decomposed by sulphuretted hydrogen; the liquid filtered from the sulphide of lead is concentrated to half its bulk; and the gum is precipitated with alcohol of 98 p. c. It contains 44.45 p. c. C., 6.31 H., and 49.24 O. (Willigk, *Wien. Akad. Ber.* 5, 190.)

3. *Gum from fermented Mangold-wurzel Juice.*—The juice is precipitated with alcohol; the precipitate washed and dissolved in water; the solution precipitated with basic acetate of lead; the precipitate decomposed under water with sulphuretted hydrogen; and the filtrate evaporated to dryness over the water-bath. — Transparent, vitreous, scarcely coloured mass, resembling gum-arabic. Contains 40.89 p. c. C., 6.10 H., and 53.01 O. (Kircher, *Ann. Pharm.* 31, 337.)

**Metagummic Acid.**

A. GÉLIS. *Compt. rend.* 44, 144; *N. J. Pharm.* 31, 216; *J. pr. Chem.* 71, 378.

FREMY. *Compt. rend.* 50, 124; *N. J. Pharm.* 37, 81; *abstr. Chem. Centr.* 1860, 607.

See page 193.

Perhaps a *pectous* modification of arabic acid. (Graham).

The acid in combination with lime forms *Cerasin*, the constituent of cherry, plum, apricot, peach, and almond tree gum, which is insoluble in water, and, according to Fremy and Gélis, is identical with the insoluble compound formed from gum-arabic.

Cherry tree gum is a mixture of arabin and cerasin in variable proportions (Schmidt); it contains 34.9 p. c. cerasin, 52.1 p. c. arabin, and from 1 to 3 p. c. ash and water. (Guérin-Varry.) *Gummi Cerasorum* boiled with water leaves a residue of bassorin-jelly, whereas *Gummi Persicorum* dissolves almost completely. Both contain a certain quantity of glucose, the latter also tannic acid. (Ludwig, *N. Br. Arch.* 82, 152). Almond tree gum is almost wholly soluble in water. (Landerer,

*Rept.* 56, 82.)—The gum of the cherry tree and of the other trees above-mentioned exhibits the same composition, nearly agreeing with the formula  $C^{12}H^{10}O^{10}$  (Guérin-Varry). When cherry tree gum is evaporated with water and hydrochloric acid, alcohol added to the solution, which has become mobile, throws down a gum containing 44.26 p. c. C., 6.27 H., and 49.47 O., therefore  $C^{12}H^{10}O^{10}$ . (Schmidt, *Ann. Pharm.* 51, 38.)

*Formation and Preparation.* 1. When oil of vitriol is covered with a layer of a syrupy solution of gum-arabic, the gum is converted into metagummic acid, which may be removed, washed and dried (Fremy).—2. Gum-arabic heated for some time to  $150^{\circ}$  becomes insoluble in water (Gélis), and is converted into metagummate of lime. (Fremy, see pp. 194, 198.)—3. Gum-arabic undergoes the same transformation when roasted with oxalic acid. (Fremy.)—4. Neubauer's arabin is rendered insoluble in water by drying, doubtless from conversion into metagummic acid.

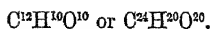
Cerasin is obtained from cherry tree gum by dissolving out the arabin with water, at  $20^{\circ}$ , and drying the undissolved portions over the water-bath. As thus prepared it is a colourless, semi-transparent, very friable mass, which contains 8.4 p. c. water and leaves 1 p. c. ash. It swells up in cold water without dissolving. (Guérin-Varry, *Ann. Chim. Phys.* 49, 274.)

Metagummic acid prepared from gum-arabic with oil of vitriol contains on the average, 40.96 p. c. C., 6.02 H., and 53.02 O. (Fremy.) Its formula is  $C^{12}H^{11}O^{11}$ , as appears from Neubauer's analysis of arabin (more correctly, that of metagummic acid. Kr. see page 197.)

Metagummic acid is not altered by boiling with water, but when boiled with alkaline water, or with a small quantity of lime, it is converted into an arabate of the alkali or of lime. (Fremy.) In like manner, natural cerasin—in so far as it contains lime—(Guérin-Varry) and metagummate of lime obtained by heating gum-arabic (Gélis), are dissolved by boiling with water. Natural cerasin likewise dissolves more easily when boiled with water, after addition of an alkaline carbonate, and with separation of carbonate of lime. (Fremy.)—Cerasin boiled with *nitric acid* of sp. gr. 1.139 yields as much mucic acid as gum-arabic. (Guérin-Varry.)

Insoluble in *alcohol*.

## Bassorin.



GUÉRIN-VARRY. *Ann. Chim. Phys.* 40, 248 and 51, 222.

MULDER. *J. pr. Chem.* 15, 207; further, 37, 338.

SCHMIDT. *Ann. Pharm.* 51, 29.

LUDWIG. *N. Br. Arch.* 82, 33 and 153.

*Traganthstoff* (Buchholz), *Traganthin*, *Adraganthin*, *Berzelius' Vegetable Mucus* in part.—The part of Bassora-gum, gum-tragacanth, and other gums, which is insoluble in water and swells up therein.

*Sources.* In *Bassora* or *Kutera gum* which, according to Vauquelin and Fremy, consists almost wholly of it, according to Guérin-Varry, of 61·31 p. c. bassorin, together with arabin, ash and constituents soluble in alcohol. See, on this subject, Guérin-Varry, Guibourt (*J. Chim. méd.* 8, 419; *Ann. Pharm.* 9, 225), Vauquelin (*Bull. Pharm.* 3, 52), Ludwig (*N. Br. Arch.* 82, 32).—In *Acajou-gum* (Trommsdorff, *N. Tr.* 22, 2, 252).—In the gum of *Cactus opuntia* (Bazin & Guibourt, *J. Pharm.* 20, 525; Trommsdorff, *N. Tr.* 19, 2, 35).—In *Gummi Simarubæ* (Ludwig).—In *false gum-tragacanth* (N. v. Esenbeck, *Mag. Pharm.* 25, 241; Brandes, *Mag. Pharm.* 33, 4).—*Gum tragacanth* contains, according to Buchholz (*Taschenb.* 1815, 83) 57 p. c. arabin and 43 p. c. bassorin, together with starch (but not always, according to Flaschhoff, *Br. Arch.* 21, 222.), the brown sort containing more starch than the white, and consequently turning blue with iodine (Fromberg, *Mag. Pharm.* 1826, 15, 169; Planche, *J. Pharm.* 13, 25). According to Guérin-Varry, it contains 53·3 p. c. arabin, 33·1 p. c. bassorin, 11·1 p. c. water, and 2·5 p. c. ash; according to others, little or no arabin. It leaves 3·57 p. c. ash (Löwenthal & Hausmann, *Ann. Pharm.* 89, 112); contains on the average 16·35 p. c. water (Ludwig, *N. Br. Arch.* 82, 38). Boiling alcohol extracts from tragacanth 1·36 p. c.: the solution was found to contain a bitter substance, sugar being found in it only once.—On the microscopical constituents of gum-tragacanth, see Mohr (*Bot. Zeit.* 1857, 37); Hartig (*Entwickl. d. Pflanzenk.* 39) Maschke (*J. pr. Chem.* 76, 49).

Gum-tragacanth dried at 17·5° contains 40·5 p. c. C., 6·61 H., and 52·82 O. (Hermann.) Select gum-tragacanth dried between 100° and 110° contains 45·25 p. c. C., 6·00 H., and 48·75 O., after deduction of 1·75 p. c. ash. (Schmidt.)

*Preparation.* Gum-tragacanth or Bassora-gum is exhausted with cold water, and the insoluble residue is dried. (Guérin-Varry.) Trommsdorff employs acajou-gum, and washes the residue likewise with alcohol.

Schmidt pours cold water on lumps of pure gum-tragacanth; leaves them to stand for 24 hours; agitates the swollen mass with alcohol containing hydrochloric acid, till it cakes together; decants the alcohol from the lumps; suspends them in water; again agitates with alcohol containing hydrochloric acid,—and so forth, till the liquid which runs off no longer leaves any residue; then removes the adhering acid by washing with alcohol, and dries the residue on glass plates. The product thus obtained must contain arabin, if that substance was present in the tragacanth. (Kr.)

*Properties.* Colourless, semitransparent, difficultly friable gum; when prepared from tragacanth, it forms dirty white scales. (Guérin-Varry.) Inodorous and tasteless. Permanent in the air.—See also Maschke (*J. pr. Chem.* 76, 48).—Not digestible. (Frerichs, *Handb. Zoochem.* viii. 577.)

				Guérin-Varry.		Schmidt.		Mulder.			
				<i>a.</i>	<i>b.</i>	<i>mean,</i> <i>at 110°.</i>	<i>mean,</i> <i>at 130°-140°.</i>				
12 C.....	72	...	44·44	...	37·28	...	35·79	.....	44·86	...	45·30
10 H ....	10	...	6·17	...	6·85	...	7·11	.....	6·20	...	5·85
10 O ....	80	...	49·39	...	55·87	...	57·10	.....	48·94	...	48·85
C <sup>12</sup> H <sup>10</sup> O <sup>10</sup>	162	...	100·00	...	100·00	...	100·00	.....	100·00	...	100·00

So, according to Schmidt. His bassorin still left 6.65 p. c. ash, and when further heated to  $170^{\circ}$ , lost 5.22 p. c. water, after which its composition agreed with the formula  $C^{12}H^{11}O^{11}$ . — *a.* From Bassora-gum; *b.* from gum-tragacanth, after deduction of ash =  $C^{12}H^{11}O^{11}$  (Guérin-Varry). Isomeric with arabic and metagummic acids, but differs from both (Fremy, *N. J. Pharm.*, 37, 81). According to Mulder, it is  $C^{24}H^{19}O^{19}$ ; he is of opinion that Schmidt's bassorin was most perfectly dried.

*Decompositions.* 1. Gum-tragacanth dried at  $100^{\circ}$  in a current of air, becomes yellowish when heated to  $140^{\circ}$ , loses at the same time 1.73 p. c. of its weight, and at  $150^{\circ}$  decomposes with stronger coloration (Mulder, *vid. sup.*). — 2. Gum-tragacanth yields by *dry distillation* carbonic acid and combustible gas, pyromucic acid containing a little ammonia, and leaves charcoal, together with carbonate of lime and a small quantity of phosphate. (Cruikshank.) — 3. Tragacanth-mucilage prepared with water acquires, after standing for some weeks, the odour of sour paste and butyric acid. (Guérin-Varry.) — 4. Bassorin heated with *nitric acid* yields 22.6 p. c. mucic acid and a small quantity of oxalic acid (Guérin-Varry); gum-tragacanth likewise yields mucic (saccharic?) acid, and oxalate of lime (Scheele; Laugier, *Ann. Chim.* 72, 82.) *Strong nitric acid* converts tragacanth into xylidin. (Braconnot.) It causes bassorin to swell up in the cold and when heated with it, forms a solution precipitable by alcohol; weak nitric acid dissolves bassorin only when heated, forming a solution precipitable by alcohol. (Trommsdorff.) — 5. Bassorin is not altered by cold oil of vitriol, but is carbonised when heated with it (Guérin-Varry). Tragacanth is carbonised by oil of vitriol, and yields traces of artificial tannin. (Hatchett.) — Dilute sulphuric acid dissolves bassorin on boiling, forming a crystallisable, non-fermentable sugar (Guérin-Varry), together with a gum whose aqueous solution is precipitated by alcohol and basic acetate of lead. Tragacanth swollen in cold water is converted into a mobile liquid by continued heating or evaporation with dilute sulphuric, hydrochloric, or oxalic acid, and ultimately dissolves with the exception of a few flocks; alcohol added to the filtrate throws down a white gum whilst glucose remains dissolved. The gum contains, on the average, 44.26 p. c. C., 6.25 H., and 49.49 O., Schmidt. — 6. Bassorin is converted by boiling with aqueous alkalis, into a soluble gum, which resembles gum-arabic, but differs from it in the precipitability of its solution by neutral acetate of lead (Fremy). — 7. Tragacanth-mucilage boiled with *quicklime* turns yellow at first, but becomes colourless again after two hours, whilst the precipitated lime appears yellow; the clear liquid contains a lime-salt in solution. (Zeise.)

*Combinations.* Bassorin is insoluble in *water*, even at the boiling heat, but swells up to a jelly when immersed in it. When tragacanth is softened with 1000 or 1200 pts. of water, and the dissolved portion is separated from the swollen, gummy mass, the latter, on being mixed with a large quantity of water, at length becomes sufficiently mobile to run through the filter in the form of a viscid liquid, each drop extending itself into a thread (Berzelius, *Lelvb.* 3 Aufl. 6, 407). If moist bassorin, which has not been previously dried, be boiled with water for two hours, it forms a colourless mobile solution, which, when evaporated, leaves a residue only partially soluble (Trommsdorff). According to some statements, tragacanth yields nothing to water; according to others it yields arabin (*vid. sup.*).

Bassorin dissolves readily in *hydrochloric acid*, also in aqueous

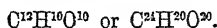
*ammonia*, and remains unaltered when the solvent is evaporated. (Trommsdorff).

*With Oxide of Lead.*—Tragacanth-jelly, diluted with a large quantity of water, coagulates with basic acetate of lead, slightly with the neutral acetate. When powdered tragacanth is macerated for twenty-four hours with cold water, the liquid strained through linen—only a small quantity of adventitious matter then remaining on the filter—then precipitated with ammonia and neutral acetate of lead, and the precipitate washed and dried at  $100^{\circ}$ , the product *a* is obtained. When uncomminuted tragacanth is macerated in water for twenty-four hours, the clear liquid poured off, two similar extracts prepared from the residue, and each precipitated with basic acetate of lead, the precipitates *b*, *c*, and *d* are obtained (Mulder). As the organic substance of all these precipitates has nearly the same composition, Mulder concludes that tragacanth does not contain arabin, but only a certain constituent, which, according to him, is pectic acid.

	Mulder.			
	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
PbO.....	51.38	53.31	38.84	47.54
C.....	17.49	20.77	27.22	23.14
H.....	2.06	2.50	3.12	2.78
O.....	29.07	23.42	30.82	26.54
	100.00	100.00	100.00	100.00

Tragacanth-jelly curdles a solution of *bichloride of tin*; according to Bostock it forms a reddish precipitate with *mercurous nitrate*; according to Pfaff, a white precipitate with both *mercurous* and *mercuric nitrate*. It is precipitated by *alcohol*.

## Vegetable Mucilage.



LEO MEIER. *Berl. Jahrb.* 27, 2, 75.

GUÉRIN-VARRY. *Ann. Chim. Phys.* 49, 248; *Schw.* 65, 220; *N. Tr.* 26, 2, 155; abstr. *Pogg.* 29, 50.

MULDER. *J. pr. Chem.* 15, 293; further, 37, 334.

SCHMIDT. *Ann. Pharm.* 51, 29.

NÄGELI & CRAMER. *Pflanzenphys. Untersuchungen*, Zürich, 1855; abstr. *Pharm. Centr.* 1855, 426.

*Gelin, Mucus; Vegetabilische Gallerte, Pflanzenschleim.*—Chiefly investigated by Schmidt; formerly confounded by Mulder with pectic acid. The substances here brought together under the name, vegetable mucilage, exhibit certain diversities of character, which may perhaps render it necessary to subdivide them. Schmidt likewise regards tragacanth, and perhaps therefore bassorin in general, as vegetable mucilage.

*Sources.* Doubtless a universally diffused constituent of plants. Described and examined, as obtained from the following parts of plants: From the roots of marsh-mallow (*Althaea officinalis*), the tubers

of various species of *Orchis* (*Salep mucilage*).—From the seeds of *Plantago Psyllium* (flea-wort), of *Linum*, of various species of *Salvia* and other *Labiatae*, and of quinces.—From the bark and leaves of the lime and elm.—From *Spharococcus crispus*, the mucilage forming nearly the entire alga, and from *Fucus saccharinus*.

On marsh-mallow mucilage, see also Trommsdorff (*N. Tr.* 19, 1, 164); on the mucilage of flea-wort seed, Braconnot, (*J. Chim. méd.* 17, 513; *Repert.* 75, 190); on linseed mucilage, Vauquelin (*Schw. J.* 9, 142) on elm and lime mucilage, Braconnot (*N. Ann. Chim. Phys.* 17, 352); on the mucilage of diseased elms, also Vauquelin (*Ann. Chim.* 21, 43).—On the mucilage of *Fucus saccharinus*, Witting, Jun. (*J. pr. Chem.* 73, 138).

**Preparation.** The undivided seed of flax, flea-wort, or quinces, is macerated, with agitation, in cold water; the liquid is strained, boiled up, again strained, concentrated in the water-bath till alcohol precipitates tenacious threads from it, then mixed with alcohol; and the precipitate is strongly pressed, left to swell up to a certain extent in water, and agitated with alcohol containing hydrochloric acid, as long as lime-salts are thereby removed. (Schmidt, Mulder.)—Earlier statements about vegetable mucilage relate chiefly to the decoction of certain parts of plants evaporated down, or exhausted with alcohol, or again boiled with animal charcoal.

**Properties.** After drying it forms a horny or cartilaginous, amorphous, and generally colourless mass. Friable. Neutral.

					Schmidt.	Mulder.	
					at 100°—110°.	from Linseed. at 150°.	from Quinces. at 130°—150°.
12 C	....	72	....	44.44	.... 44.43 to 44.95	.... 44.83	.... 45.45
10 H	....	10	....	6.16	.... 6.12 to 6.33	.... 5.92	.... 6.07
10 O	....	80	....	49.40		.... 49.25	.... 48.48
$C^{12}H^{10}O^{10}$					162	.... 100.00	100.00

		Nägeli & Cramer.	
		from Linseed.	from Quinces.
C	.....	44.90	46.60
H	.....	6.03	6.11
O	.....	49.07	47.29
100.00		.....	100.00

Schmidt's and Mulder's analyses give the composition of the mucilage after deducting the ash, which, in Schmidt's substance amounted to 0.415—1.39 p.c., and in Mulder's to 2.04—4.25 p.c.—Schmidt examined mucilage from marsh-mallow, flea-wort, *Spharococcus crispus*, linseed, and quinces, with nearly equal results.—Mulder gives the formula  $C^{24}H^{19}O^{19}$ , and supposes that Schmidt's substances were not sufficiently dried. The larger amount of ash in Mulder's substances may perhaps be explained by the smaller amount of water that he found. For Guérin-Varry's analysis, and his partly unintelligible statements, see *Ann. Chim. Phys.* 49, 248.

**Decompositions.** 1. Linseed mucilage dried at 100° in a stream of air, loses 1.28 p.c. of its weight when gradually heated to 150°, and forms a trace of acid; when further heated to 170°, it diminishes in weight by 1.03 p.c. more, at the same time, however, exhibiting marks of decomposition. Quince mucilage loses 0.65 p.c. at 150°, and 1.04 p.c. more at 170°. The mucilage of flea-wort seed, dried at 110°, loses 5.8 p.c. at 175°; quince-seed mucilage 4.96 p.c. (Schmidt.)—

2. Marsh-mallow mucilage yields, by *dry distillation*, carbonic acid and carburetted hydrogen, a distillate of empyreumatic oil and acid water (containing ammonia) and a residue of charcoal. (Leo Meier.)—  
 3. Vegetable mucilage boiled with dilute *acids* becomes mobile and is resolved into gum and sugar. Quince mucilage is at first coagulated by acids, and decomposed after a few hours; the mucilage of flea-wort and other plants is more easily decomposed. When salep-tubers, cut into small pieces, are left to swell up in water, then crushed and digested for some time with dilute sulphuric acid, cellular membrane is left behind, and the filtered liquid contains gum and sugar. (Schmidt.)—

4. Mucilage, boiled with *nitric acid*, yields oxalic acid, and, according to older statements, likewise mucic acid. Marsh-mallow mucilage, treated with nitric acid, yields oxalic acid (Meier); mucic acid (Trommsdorff). Flea-wort mucilage yields oxalic acid and artificial bitter, without mucic acid. (Braconnot.) Linseed mucilage, obtained by exhausting the seed with water, and evaporating the extract, is decomposed by water into a soluble and an insoluble portion, the latter only yielding mucic acid with nitric acid. (Guérin-Varry.) According to Vauquelin and Meier, linseed mucilage treated with nitric acid, yields oxalic acid, artificial bitter and mucic acid; according to Nägeli & Cramer, the chief products are oxalic acid, and a crystalline powder, nearly insoluble in dilute nitric acid and in water, moderately soluble in aqueous potash. Quince mucilage yields with nitric acid nothing but oxalic acid (Nägeli & Cramer); so likewise elm-mucilage (Braconnot). — With strong nitric acid, linseed-mucilage yields a small quantity of xyloidin. (Braconnot.) — Vegetable mucilages heated with nitrosulphuric acid yield a detonating product. (Nägeli & Cramer.)

5. Vegetable mucilage heated with *oil of vitriol* is charred, with evolution of sulphurous acid. (Meier.) Quince-mucilage treated with oil of vitriol is coloured blue by *iodine* (Kützing, Nägeli & Cramer), and splendid red after a few days by *biniodide of zinc*. (Nägeli & Cramer.)

6. Elm-mucilage thickened by *potash-ley*, becomes fluid again on boiling, and is converted into gum. (Braconnot.)— 7. Mucilage is decomposed by digestion with *wheat-glutin* in the same manner as by dilute acids. (Schmidt.) It is not altered by *saliva*, *gastric juice*, *bile*, or *pancreatic juice*. (Frerichs, *Handb.* viii. *Zoochem.* 577.)

Vegetable mucilage swells up strongly when *water* is poured upon it, but, according to Nägeli & Cramer, it does not form a true solution. The resulting jelly is impervious to alcohol, ether, and oils both fixed and volatile. Dry linseed mucilage is but partially soluble in water. Quince-mucilage also does not dissolve in water, either cold or hot, during washing, if it has been precipitated from its aqueous solution by acids. (Schmidt.) The aqueous solution of some vegetable mucilages solidifies in a gelatinous mass; that of others does not. On the swelling power of quince-mucilage, see Nägeli & Cramer.

The aqueous solution of flea-wort mucilage is not altered by dilute acids, but quince mucilage is coagulated by *acids*, *alkalis*, and many *salts*. (Schmidt.) From the mucilage of *Fucus saccharinus*, nitric acid and dilute sulphuric acid separate white flocks. (Watting, *J. pr. Chem.* 73, 138). — *Iodine* colours vegetable mucilage greenish yellow.



*Baryta-water* coagulates marsh-mallow mucilage (Trommsdorff, flea-wort mucilage (Braconnot), elm mucilage (Berzelius). *Line-water* acts in a similar manner. Salep mucilage boiled with weak potash-ley forms a clear jelly after addition of a small quantity of chloride of calcium. (Schmidt.) Vegetable mucilage is not thickened by borax (Schiller, *Berl. Jahrb.* 1808, 186, and others).

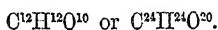
Vegetable mucilage is not precipitated, at least not completely, by *neutral acetate of lead*; but the basic acetate produces complete precipitation. See Mulder's analysis of the lead precipitates. (*J. pr. Chem.* 15, 293.) The mucilage of *Fucus saccharinus* is precipitated by neutral acetate of lead. (Witting).

Vegetable mucilage is not altered by *cupric* or *ferric sulphate*.

It is insoluble in *alcohol*, and is precipitated from its aqueous solution by *tincture of galls*.

### Saccharoidal Substances $C^{12}H^{12}O^{10}$ .

#### Pinite.



BERTHELOT (1855). *N. Ann. Chim. Phys.* 46, 76; *Compt. rend.* 41, 392; *J. pr. Chem.* 67, 233; *Chem. centr.* 1855, 699. — *Chim. org.* Paris 1860, 2, 213.

JOHNSON. *Sill. Am. J.* [2], 22, 6; *J. pr. Chem.* 70, 245; *N. Br. Arch.* 93, 54; *Chem. Centr.* 1856, 765.

*Pine-sugar*; *Fichtenzucker*.

*Occurrence.* In the sap of the *Pinus lambertina* of California. This liquid exudes from the stems, collects in cavities made with fire at the bottom of the stems, and hardens into roundish masses. (Berthelot.)

*Preparation.* From the crude hardened juice:—1. By dissolving it in water, decolorising the solution with animal charcoal, leaving the filtered liquid to evaporate, and recrystallising from cold water. The crystals do not separate till the solution has stood for several weeks, and they are slow of growth. (Berthelot).—2. The hot alcoholic solution is decolorised with animal charcoal and mixed with ether till turbidity ensues. After a few hours crystals appear, which may be purified by recrystallisation. (Johnson.)

*Properties.* Hard colourless, radiate nodules, consisting of microscopic, imperfectly developed crystals. Melts above  $150^{\circ}$ . In vacuo, near the boiling point of mercury, it forms white fumes without distilling. Its taste is almost as sweet as that of sugar-candy. Sp. gr. 1.53. Rotatory power  $[\alpha]_D = 58.6^{\circ}$  to the right. Neutral. (Berthelot.)

				Berthelot.	Johnson.
12 C .....	72	...	43·9	...	43·5
12 H .....	12	...	7·3	...	7·5
10 O .....	80	...	48·8	...	49·0
				...	49·85
$C^{12}H^{12}O^{10}$ .....	164	...	100·0	...	100 0
				...	100·00

*Decompositions.* 1. Pinite heated above  $150^{\circ}$  gives off empyreumatic water; at  $250^{\circ}$  it is partly converted into a black insoluble mass, but it is only at a higher temperature that complete decomposition takes place, an odour of caramel being emitted, and tarry products distilling over. — 2. Heated on *platinum foil*, it chars and burns away completely. — 3. Hot *nitric acid* decomposes it, with formation of nitro-compounds, and a small quantity of oxalic acid. — 4. Pinite blackens when *oil of vitriol* is quickly poured upon it, but dissolves if gradually brought in contact with the acid at a moderate heat, apparently forming pinisulphuric acid, the soluble lime-salt of which decomposes when its solution is evaporated. — *Dilute sulphuric acid* does not affect pinite even at the boiling heat. — 5. Heated with *tartaric acid* to  $100^{\circ}$ — $120^{\circ}$  in sealed tubes for five hours, it yields pin tartaric acid; with *benzoic acid* at  $200^{\circ}$ — $250^{\circ}$ , it yields benzo-pinite; with *stearic acid* at  $200^{\circ}$ — $250^{\circ}$ , stearo-pinite. — 6. When its concentrated aqueous solution is brought in contact with *biniodide of phosphorus*, it becomes partially carbonised, and yields a volatile, strongly refracting oil, smelling of acetone, carbolic acid, and salicylic acid. — 7. When very strongly heated with lumps of *potash* or with lime, it is decomposed with evolution of acrid fumes. — 8. It reduces the hot aqueous solution of *nitrate of argentammonia*. Pinite is not altered by *aqueous potash*, *ammonia* or *baryta*, by *potassio-cupric tartrate* or *sesquichloride of iron*. It does not ferment with *yeast*.

*Combinations.* Pinite is very soluble in *water*. It dissolves abundantly in *fuming hydrochloric acid*, and crystallises somewhat coloured on cooling.

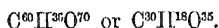
The aqueous solution of pinite dissolves *lime* more freely than pure water.

*Lead-compound.*—From a concentrated aqueous solution of pinite, ammoniacal sugar of lead throws down a white, curdy, very flocculent precipitate, which when recently precipitated dissolves in a larger quantity of cold water, but is only partially dissolved, and decomposed at the same time, by boiling water.

				At $100^{\circ}$ in vacuo.	Berthelot.
12 C .....	72	...	11·8	...	12·5
12 H .....	12	...	2·0	...	2·1
10 O .....	80	...	13·1	...	12·6
4 PbO .....	446·8	...	73·1	...	72·8
$C^{12}H^{12}O^{10}, 4PbO$ .....	610·8	...	100·0	...	100·0

Aqueous pinite dissolves *neutral acetate of lead*.

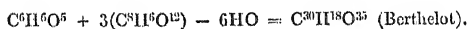
Pinite is nearly insoluble in *absolute alcohol*, slightly soluble in *boiling alcohol of ordinary strength*. (Berthelot.)—Soluble in boiling alcohol (Johnson).—Insoluble in *chloroform*. (Berthelot.)

*Conjugated Compounds of Pinite.***Pini-tartaric Acid.**

BERTHELOT. (1857.) *N. Ann. Chim. Phys.* 54, 84; abstr. *Compt. rend.* 45, 268; *Chem. Gaz.* 1857, 441; *J. pr. Chem.* 73, 159.

*Pinit-tartarsäure. Acide pinitartrique.*

Formed, like dulci-tartaric acid, from 1 at. pinite and 3 at. tartaric acid.



*Lime-salt.*—Gives off 16·8 p. c. water at 100°.

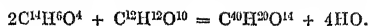
	at 100°.			Berthelot.		
60 C.....	360	....	30·5	....	29·6	
42 H .....	42	....	3·5	....	3·6	
76 O.....	608	....	51·7	....	51·0	
6 CaO .....	168	....	14·3	....	15·8	
<hr/>						
$C^{60}H^{30}Ca^6O^{70}, 12HO$ .....	1178	....	100·0	....	100·0	

**Benzo-pinite.**

BERTHELOT. *Chimie organique*, Paris, 1860, 2, 206.—*Compt. rend.* 41, 452.

A. *Mono-acid.*—*Pinite monobenzoïque.*— $C^{60}H^{20}O^{14}$ .

Pinite is heated with benzoic acid in a sealed tube for some hours to 200°—250°; the excess of benzoic acid is saturated with aqueous carbonate of potash and finally with a small lump of solid caustic potash; the liquid is mixed with an equal quantity of ether; and the supernatant ethereal solution is decanted, after standing quietly for a while, then treated with bone-black, and evaporated, first over the water-bath, afterwards in a strongly heated sand-bath:

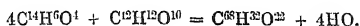


Solid resin. Neutral. *Hydrochloric acid* gas passed through its solution in absolute alcohol resolves it into benzoate of ethyl and slowly crystallising pinite. By *lime* at 100°, it is slowly converted into pinite and benzoate of lime.—Insoluble in *water*.—Soluble in *absolute alcohol* and in *ether*. (Berthelot).

B. *Bi-acid.*—*Pinite dibenzoïque.*— $C^{60}H^{32}O^{22}$ .

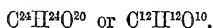
Monobenzo-pinite is heated to 200°—250° with benzoic acid, and

the product is freed from excess of benzoic acid in the same manner as A :



Solid. Neutral. Insoluble in *water*. Soluble in *ether*. (Berthelot.)

### Quercite.



BRACONNOT. (1849.) *N. Ann. Chim. Phys.* 27, 392; *J. pr. Chem.* 49, 232; *Pharm. Centr.* 1850, 92.

DESSAIGNES. *Compt. rend.* 33, 308 and 462; *Ann. Pharm.* 81, 103 and 251; *Pharm. Centr.* 1861, 746 and 959.

*Sugar of Acorns.*—The name *quercin* was given by Scattergood (*Repert.* 34, 146) to crystals from *Quercus falcata*; by Gerber (*N. Br. Arch.* 34, 167) to crystals from oak-bark, the nature of which was not determined.

Discovered by Braconnot in the fruit of *Quercus racemosa* and *Q. sessiliflora* (*Handb. viii., Phytochem.* 77); recognised as a peculiar substance, and investigated by Dessaignes.

*Preparation.* The aqueous extract of bruised acorns is freed from dissolved tannic acid by heating it with lime; the filtrate is left to ferment with yeast, to remove the fermentable sugar, which hinders the separation of the quercite; the liquid, after filtration, is evaporated to a syrup, and the crystals, which separate from it after a while, are washed with cold alcohol, and recrystallised from water or weak spirit. (Dessaigues, *N. J. Pharm.* 251, 30.)

*Properties.* Hard crystals, grating between the teeth, permanent in the air. They belong to the oblique prismatic system. Rhombic prism *u*. (*fig.* 99), having the obtuse edge truncated by *t* (*fig.* 97); above, it has also the oblique end-face *i*, and below, the face *f* (*fig.* 94), and the oblique prism *z*. The faces *u* are vertically striated. The faces are unequally developed. *u* : *u* in front =  $106^{\circ} 30'$ ; *u* : *t* =  $143^{\circ} 15'$ ; *t* : *i* =  $111^{\circ} 3'$ ; *t* : *f* =  $122^{\circ} 40'$ ; *i* : *f* behind =  $126^{\circ} 17'$ , by calculation, =  $126^{\circ} 38'$  (nearly) by observation; *z* : *z* over *i* =  $108^{\circ} 52'$  by calculation, =  $109^{\circ} 5'$  by observation; *z* : *i* =  $144^{\circ} 26'$  by calculation, =  $144^{\circ} 28'$  by observation; *u* : *i* =  $106^{\circ} 44'$  by calculation, =  $106^{\circ} 15' - 50'$  by observation; *u* : *f* =  $115^{\circ} 37'$  by calculation, =  $115^{\circ} 15'$  (nearly) by observation (Sénarmont, *Rammelsberg's Handbuch*, 224). — Permanent at  $215^{\circ}$ , melts at  $235^{\circ}$ , and partly sublimes, a small portion of the residue becoming carbonised. (Dessaigues.)

		Dessaigues.			
		<i>a.</i>		<i>b.</i>	
24 C .....	144	43.90	43.74	43.69	
24 H .....	24	7.31	7.53	7.71	
20 O .....	160	48.79	48.73	48.60	
$\text{C}^{24}\text{H}^{24}\text{O}^{20}$ .....	328	100.00	100.00	100.00	

*a.* From nitroquercite (Dessaigues).

*Decompositions.* 1. Converted by hot *nitric acid* into oxalic acid, not into mucic acid (Braconnot, Dessaignes).—2. Triturated with *oil of vitriol*, it forms a colourless solution containing a conjugated acid, whose lime-salt does not crystallise.—3. *Nitrosulphuric acid* converts it into nitroquercite. (Dessaignes.) Nitroquercite is a white amorphous resin, insoluble in water, soluble in hot alcohol; treated in alcoholic solution with sulphuretted hydrogen, it is reduced to quercite, with separation of sulphur. (Dessaignes, *Compt. rend.* 33, 462; *Ann. Pharm.* 81, 251.)—Heated with *tartaric acid*, it forms quercitartaric acid (Berthelot, *Compt. rend.* 45, 268); with *benzoic* and *stearic acids*, it forms benzo-quercite and stearo-quercite. (Berthelot, *Chim. org.* 2, 209.)

Not altered by boiling potash-ley, or by cupracetate of potash; does not ferment with yeast or with cheese (Dessaignes).

*Combinations.* Soluble in from 8 to 10 pts. of cold water. Aqueous quercite dissolves a small quantity of lime.

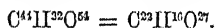
*With Baryta.*—When 2 at. quercite ( $C^{24}H^{24}O^{10} = 1$  at.) and 4 at. baryta are dissolved together in water, a large quantity of hydrate of baryta crystallises out on cooling, and an additional quantity on addition of alcohol; after the removal of this deposit, there remains a gummy solution which does not crystallise in vacuo.—After drying in vacuo, it contains 29.41 p. c. baryta and gives off 5.92 p. c. water at  $150^{\circ}$ , and is probably therefore  $C^{24}H^{24}O^{20}, 2BaO + 4H_2O$  (calc. 29.59 p. c. BaO, 6.96 p. c.  $H_2O$ ). (Dessaignes.)

From a warm solution of *basic acetate of lead* mixed with ammonia, aqueous quercite throws down a copious white precipitate, which also does not become crystalline on cooling. (Dessaignes.)

Quercite dissolves in hot weak *spirit*.

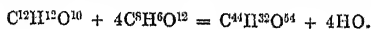
### Conjugated Compounds of Quercite.

#### Querci-tartaric Acid.



BERTHELOT. (1857.) *N. Ann. Chim. Phys.* 54, 82; abstr. *Compt. rend.* 45, 268; *N. J. Pharm.* 33, 95; *Chem. Gaz.* 1857, 441; *J. pr. Chem.* 73, 159.

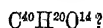
Obtained, like dulci-tartaric acid, from quercite and tartaric acid.



*Quercitartrate of Lime* gives off 16.1 p. c. water at  $110^{\circ}$ . (Berthelot.)

at $100^{\circ}$ .		Berthelot.	
44 C.....	264 ....	30.0 ....	31.0
30 H.....	30 ....	3.4 ....	3.9
52 O.....	416 ....	47.4 ....	47.3
6 CaO .....	168 ....	19.2 ....	17.8
$C^{44}H^{32}Ca^6O^{54}, 4H_2O$ .....	878 ....	100.0 ....	100.0

## Benzo-quercite.



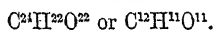
BERTHELOT. *Chim. org.*, Paris, 1860, 2, 220. — *Compt. rend.* 44, 452.

*Benzöesaure-Quercit, Benzoessäure-Quercitester; Quercite benzoïque.*—

Prepared, like monobenzo-pinite, by heating quercite with benzoic acid for several hours, in sealed tubes, to about 200°. — Solid, neutral. — Dissolved in absolute alcohol and treated with *hydrochloric acid gas*, it is resolved into quercite and benzoate of ethyl. — Insoluble in water, soluble in ether. (Berthelot.)

Carbo-hydrates  $C^{12}H^{11}O^{11}$ .

## Milk-sugar.



- LICHTENSTEIN. (1772.) *Abhandl. vom Milchzucker*. Braunsch. 1772.  
 CRUIKSHANK. *Scher. J.* 3, 293.  
 HERMSTADT. *Crell. N. Entd.* 5, 31.  
 BOUILLON-LAGRANGE & VOGEL. *J. Phys.* 72, 208; *Schw.* 2, 342; *Gill.* 42, 135.  
 BERZELIUS. *Ann. Chim.* 95, 67.  
 BAUMANN. *N. Br. Arch.* 37, 47.  
 HAGEN. *Pogg.* 71, 532; *J. pr. Chem.* 42, 470.  
 A. BENSCH. *Ann. Pharm.* 61, 221.  
 POGGIALE. *Compt. rend.* 28, 505; *N. J. Pharm.* 15, 413; *J. pr. Chem.* 47, 13; *J. Chim. méd.* 25, 364.  
 BRENDENCKE. *N. Br. Arch.* 78, 88.  
 KRAUSE & STÄDELER. *Mitth. d. naturf. Gesellsch. in Zürich*, 1854, 473; *Chem. Gaz.* 1855, 67; *Pharm. Centr.* 1854, 936; *Lieb. Kopp. Jahresber.* 1854, 746.  
 A. LIEBEN. *Wien. Akad. Ber.* 18, 180; *Chem. Centr.* 1856, 567; *J. pr. Chem.* 68, 407.  
 PASTEUR. *Compt. rend.* 42, 347; *Chem. Centr.* 1856, 253; *Inst.* 1856, 91; *J. pr. Chem.* 68, 427.  
 DUBRUNFAUT. *Compt. rend.* 42, 228; *Chem. Centr.* 1856, 233; *Inst.* 1856, 61; *J. pr. Chem.* 68, 422.  
 LUBOLDT. *J. pr. Chem.* 77, 282; *abstr. Rép. Chim. pure*, 2, 41; *N. J. Pharm.* 36, 306.

*Lactin* (Pasteur). *Lactose* (Dumas), but different from the lactose of Pasteur (*vid. inf.*). — Originally prepared by Fabrizio Bartholetti, in 1619, from whey, thence called *Manna* or *Nitrum seri lactis* and afterwards by Bergmann, *Galacticum Bartholetti*. Recommended as a medicine by Ludovico Testi in 1698.

*Source.* In the milk of mammalia. According to Dumas (*Compt. rend.* 21, 707) it is not found in the milk of carnivora, excepting after they have taken food containing starch or sugar; this statement is however contradicted by Bensch. Cream contains a smaller proportion of lactin than the milk from which it is obtained.

(Hoppe, *Virchow's Arch.* 17, 417.) On the quantity of milk-sugar in milk, see *Handb.* viii, *Zoochem.* 260; on the determination of milk-sugar, *ibid.* 253 et seq.; on methods of estimation by the optical rotatory power, see Poggiale (*Compt. rend.* 28, 584; *Ann. Pharm.* 52, 116).

The white of hens' eggs during incubation contains milk-sugar, according to Winckler (*Repert.* 92, 46; *Chem. Gaz.* 90, 280); not, according to Lehmann, (*Handb.* viii, *Zoochem.* 285). Braude thinks he has found lactin in chyle. (*ibid.* 221). Braconnot's lactin of acorns is quercite (p. 214).—According to Simon (*Die Frauenmilch*, Berlin 1838; abstr. *Berzelius Jahresber.* 19, 714), the sugar of human milk has a sweeter taste than ordinary milk-sugar, is less fusible, and yields with nitric acid a smaller quantity of mucic acid; in other respects it resembles ordinary milk-sugar.

**Preparation.** Milk kept in contact with rennet for the preparation of cheese coagulates, with separation of whey-cheese. The whey separated therefrom, if evaporated to the consistence of honey, yields, after standing for some time in a cool place, a crystalline deposit of milk-sugar, which may be purified by repeated solution in water, clarification and crystallisation, finally (according to Städeler & Krause) by repeatedly precipitating the aqueous solution with alcohol.

For the detection of milk-sugar, milk, diluted with 3 pts. water, is heated to boiling with a few drops of acetic acid; the liquid is filtered; the filtrate mixed with carbonate of magnesia and evaporated; the dry residue treated with alcohol to remove all matters soluble therein; and the undissolved portion exhausted with hot water: on evaporating this last-mentioned solution to a syrup, the milk-sugar crystallises out.

**Properties.** See *Hydrated milk-sugar*. Crystallised milk-sugar, heated continuously to  $140^{\circ}$ — $145^{\circ}$ , is converted, with loss of 1 at. water, into anhydrous milk-sugar. (Städeler & Krause.) Dextro-rotatory power  $[\alpha]_D^{20} = 59.3^{\circ}$  (Berthelot),  $= 60.28$  (Biot, *Compt. rend.* 42, 349).

at $140^{\circ}$ — $150^{\circ}$ .			Städeler & Krause. Lieben.		
12 C.....	72	...	42.11	.....	41.95
11 H.....	11	...	6.43	.....	6.51
11 O.....	88	...	51.46	.....	51.54
$C^{12}H^{10}O^{11}$ .....	171	...	100.00	.....	100.00

So according to Städeler & Krause. Earlier formulæ for (crystallised) milk-sugar:  $C^{10}H^8O^8$  (Berzelius),  $C^{12}H^{10}O^{12}$  (Liebig),  $C^{24}H^{20}O^{20}, 5H_2O$  or  $C^{12}H^{10}O^{10}, 2H_2O$ , according to others. Berzelius regarded milk-sugar fused with loss of 10 p.c. water as anhydrous.

**Decompositions.** 1. Milk-sugar dried at  $150^{\circ}$  acquires a yellow colour at  $160^{\circ}$ , emits an odour of caramel (Städeler & Krause), and diminishes slightly in weight. Heated to  $175^{\circ}$ , or above, it is partly converted, with loss of weight (amounting to 13 p.c. of the crystallised substance), into a mixture of lacto-caramel and a substance insoluble in water which then melts at  $203.5^{\circ}$ . (Lieben.)

Crystallised milk-sugar when carefully heated, melts, gives off 12 p.c. water, and solidifies on cooling to a crystalline mass, which, when dissolved in water, regains the water of crystallisation that it had lost. (Berzelius.) When melted, it gives off 13.3 p.c. water and leaves a brown mass. (Vauquelin, *Bull. Pharm.* 3, 49.) Milk-sugar when roasted, becomes brown and tough, and is converted into a mixture of  $\frac{1}{4}$  saccharic acid and  $\frac{3}{4}$  gum (Schill, *Ann. Pharm.* 31, 152), into caramel. (Vauquelin.) The brown product formed by heating milk-sugar yields mucic acid with nitric acid, the same as unaltered milk-sugar. (Géllis, *N. Ann. Chim. Phys.* 52, 355.)

2. Milk-sugar yields, by *dry distillation*, carbonic acid and combustible gases, aqueous acetic acid, empyreumatic oil, and charcoal. (Cruikshank.) — The acid watery distillate amounts to 61 p. c., is less mobile than that obtained from cane-sugar, and more abundantly precipitated by alcohol. (Vauquelin.) — 3. Milk-sugar heated in the *open fire*, swells up, becomes brown and tenacious, gives off the odour of burnt sugar, and burns with a white flame, leaving a large quantity of charcoal. (Bouillon & Vogel.)

4. When *oxygen gas* is passed over milk-sugar mixed with spongy platinum, the milk-sugar is completely resolved into carbonic acid and water. (Reiset & Millon, *N. Ann. Chim. Phys.* 8, 285.) Milk-sugar is not altered by *ozone*. (Gorup-Besanez, *Ann. Pharm.* 110, 86.)

5. The aqueous solution of milk-sugar heated in a sealed tube turns yellow and finally dark brown, and if afterwards left to evaporate, leaves an acid deliquescent syrup, which does not crystallise even after several months. The decomposition takes place slowly at 100°, more quickly at 130°; between 105° and 110° it takes place, even if the air is completely excluded and replaced by hydrogen. If the air has access, oxygen is absorbed, and (a smaller volume of) carbonic acid is evolved. (F. Hoppe, *Chem. Centr.* 1860, 54.) Vohl (*Ann. Pharm.* 105, 334) found that when a concentrated solution of milk-sugar was heated in a sealed tube to nearly 200° and then left to cool, the brown liquid no longer yielded with alcohol a precipitate of milk-sugar, but when mixed with a larger quantity of alcohol, it deposited crystals of grape-sugar [lactose?]. — A concentrated solution of milk-sugar remains unaltered at ordinary temperatures if the air is excluded; but if exposed to the air, it turns acid in the course of a year and yields grape-sugar. (Lieben.)

6. Milk-sugar distilled with *bichromate of potash* and *sulphuric acid* yields aldehyde. (Guckelberger, *Ann. Pharm.* 64, 98.)

7. Aqueous milk-sugar distilled with *iodine* and bicarbonate of potash, yields iodoform (Millon, *Compt. rend.* 21, 828; *J. pr. Chem.* 37, 53). — 7 a. When a mixture of 1 at. milk-sugar, 4 at. bromine, and water is heated to 100° in a sealed tube, the liquid becomes colourless, and, on opening the tube, carbonic acid and hydro-bromic acid escape, with the odour of bromide of ethyl. The residual brominated product is strongly acid, decomposes with evolution of bromine when heated, and cannot be obtained pure. When recently precipitated oxide of silver is added to it, till the acid reaction disappears, and the liquid is then filtered, a solution free from bromine is obtained, containing a silver salt, which, when freed from silver by sulphuretted hydrogen and evaporated, leaves an acid syrup. This acid forms, with ammonia, a salt which crystallises well and is precipitated by basic acetate of lead, — with other bases, it forms uncrystallisable salts. (Hlasiwetz, *Ann. Pharm.* 119, 281.) The acid here formed is isobigly colethyleneic acid. (Barth & Hlasiwetz, *Ann. Pharm.* 122, 96; — see below p. 232.) 7 b. In *chlorine gas* milk-sugar turns red and afterwards black, giving off hydrochloric and carbonic acids. From the aqueous solution of the residue, alcohol precipitates unaltered milk-sugar. By passing chlorine gas through a warm concentrated aqueous solution of milk-sugar, a liquid containing hydrochloric acid is obtained, which deposits crystals,



having the appearance of milk-sugar, but an acid reaction. (Bouillon & Vogel.)

8. With strong *nitric acid*, milk-sugar forms, not xyloïdin, but a very bitter substance (Bracomot).—Heated with many times its weight of moderately dilute nitric acid, it is decomposed, with formation of mucic, saccharic, tartaric, oxalic and carbonic acids, and the decomposition-products of nitric acid.

When 1 pt. of milk-sugar is heated with  $2\frac{1}{2}$  pts. nitric acid of sp. gr. 1.32 and  $2\frac{1}{2}$  pts. water till it dissolves, carbonic acid is briskly evolved, together with the decomposition-products of nitric acid, and if the heating be continued, mucic acid separates. The mother-liquor, after the addition of  $\frac{1}{4}$  of the quantity of nitric acid used at the commencement, gentle boiling, and concentration, yields an additional quantity of mucic acid, the total quantity amounting to  $\frac{1}{2}$  of the weight of the milk-sugar. The remaining mother-liquors and wash-waters boiled, with frequent addition of nitric acid, as long as samples taken out turn brown when supersaturated with potash-ley, contain tartaric acid (probably formed by decomposition of the saccharic acid: *Liebig*), also oxalic acid and a small quantity of saccharic acid, which last is present in greatest quantity immediately after the separation of the mucic acid. (*Liebig, Ann. Pharm.* 113, 1.) The tartaric acid appears to exist in the nitric acid solution as metatartaric acid (x. 327), and only afterwards to be converted into crystallisable tartaric acid. (*Erdmann, J. pr. Chem.* 79, 135.) The mucic acid is produced in greatest quantity when dilute nitric acid is used and the liquid is not very strongly heated, whereas carbonic and oxalic acid are produced in proportion as the mucic acid diminishes. (*Liebig, Pogg.* 31, 349.) When nitric acid containing hydrochloric acid is heated with milk-sugar, a volatile cyanogen-compound is given off (*Liebig*).

Nitric acid acts on milk-sugar in two ways. *a.* It converts the greater part of the milk-sugar into mucic acid, which then undergoes further decomposition, yielding tartaric acid.—*b.* The smaller portion of the milk-sugar is converted by the nitric acid, as by other acids, into grape-sugar, and then (like the latter) yields saccharic acid, which also, by the continued action of the nitric acid, may be transformed into tartaric acid (*Heintz, Berl. Akad. Ber.* 1860, 263; *Chem. Centr.* 1860, 726). But dilute acids convert milk-sugar, not into grape-sugar, but into *lactose*, and this compound treated with nitric acid yields, not saccharic acid, but mucic acid in twice the quantity of that yielded under the same circumstances by milk-sugar (Kr.).

When milk-sugar is treated with nitric acid, as for the preparation of mucic acid, the dextro-rotatory power of the solution is increased to  $\frac{1}{10}$  of its original amount then diminishes and vanishes altogether, but the liquid after a while again acquires dextro-rotatory power equal to  $\frac{1}{4}$  of the original amount, which, however, likewise vanishes, if the action of the nitric acid is continued, without reappearing. (Dubrunfaut.)

When milk-sugar is heated with 1 pt. of water and  $\frac{1}{2}$  nitric acid, of 30° B., the solution, whose formation is attended with evolution of carbonic acid and nitrous gas, leaves when evaporated a yellow mass (soluble in hot but not in cold alcohol, and precipitated from the hot solution in the form of a yellow powder), which contains neither oxalic nor malic acid, and does not precipitate baryta-water, lime-water, or neutral acetate of lead. (Bouillon & Vogel.)

Heintz's view that the tartaric acid of milk-sugar proceeds from the mucic acid is incorrect, because mucic acid, which is optically inactive, yields racemic acid when treated with nitric acid, whereas milk-sugar yields dextro-tartaric acid with only a slight admixture of racemic acid (Carlen, *Compt. rend.* 53, 343).

9. *Oil of vitriol* poured upon milk-sugar colours it brown and chars it at  $100^{\circ}$ .—*Dilute sulphuric acid* leaves milk-sugar unaltered in the cold, even after several weeks' contact (Bensch), but at higher temperatures, increases its rotatory power by  $\frac{3}{10}$ , and converts it into a peculiar fermentable sugar (Pasteur's *Lactose*), and partially into a dextro-rotatory, non-fermentable substance (Dubrunfaut).—The lactose thus produced was formerly regarded as grape-sugar, till Bouchardat pointed out the difference between the two. (*Berthelot's Chim. organ.* 2, 240).—The liquid, if brought into the fermenting state at the moment when the rotatory power has increased to  $\frac{1}{10}$  of its original amount, is capable of yielding a quantity of alcohol equal to 37 per cent. of the crystallised milk-sugar; if the heating with dilute sulphuric acid be continued, no alteration of the rotatory power takes place, but the sugar decomposes. (Dubrunfaut.) According to Persoz (*J. Chim. m  d.* 9, 419; *Berz. Jahresber.* 14, 380), the rotatory power of milk-sugar is increased by addition of acids, diminished by boiling, and is smallest when the milk-sugar has become fermentable.

10. When milk-sugar is covered with *nitrosulphuric acid*, and the solution is precipitated by water, a compound (*nitrolactide*) is formed, which detonates at  $75^{\circ}$  (Reinsch), not below  $100^{\circ}$  (Vohl), crystallises from alcohol in nacreous lamin  , does not give up its crystallisation-water at  $100^{\circ}$ , but when its alcoholic solution is boiled for some time, parts with its water, takes up alcohol and becomes amorphous (Vohl, *Ann. Pharm.* 70, 368; Reinsch, *Jahrb. pr. Pharm.* 18, 102). The nitro-compounds formed from milk-sugar behave when heated like ternitro-dulcite. (B  champ, *Compt. rend.* 51, 258.)

11. With *concentrated hydrochloric acid*, milk-sugar becomes brown and black, and by boiling with the dilute acid, it is converted into ordinary sugar. (A. Vogel).—12. Triturated with *glacial phosphoric acid*, it turns red but does not carbonise (A. Vogel, *J. Pharm.* 1, 199); with moist *arsenic acid*, it burns brown. (Elsner.) With *arsenious acid* it behaves like cane-sugar. (Baumann).—13. By boiling with aqueous *iodic acid*, it is slowly oxidised. (Millon, *Compt. rend.* 19, 271).—14. When triturated with 2 pts. *chlorate of potash*, it is set on fire by oil of vitriol. (Bouillon & Vogel.)

15. *Acetic acid* does not convert aqueous milk-sugar into grape-sugar (lactose) even when heated (A. Vogel; Struckmann & B  deker, *Ann. Pharm.* 97, 152).—When milk-sugar is heated for 50—60 hours to  $100^{\circ}$ — $120^{\circ}$  with *glacial acetic acid*, *butyric acid* or *tartaric acid*, water is eliminated, and compounds are formed analogous to those produced under similar circumstances by grape-sugar. (Berthelot, *N. Ann. Chim. Phys.* 54, 82; and 60, 98.)

When tartaric acid is heated with milk-sugar and the product is treated in the manner described under "Dulcite," two compounds are obtained under slightly different circumstances. a. *Galactoso-tetratar-*

*laric acid*  $C^{44}H^{30}O^{54}$  is produced, with elimination of 5 at. water, from 1 at. milk-sugar and 4 at. tartaric acid,  $C^{12}H^{11}O^{11} + 4C^8H^6O^{12} = 5H_2O$ . The lime-salt of this acid gives off 19.2 p. c. water at  $110^\circ$ , and then contains 27.3 p. c. C, 5.2 H, and 17.2 p. c. lime, corresponding to the formula  $C^{44}H^{24}Ca^9O^{61} + 10 Aq.$  (calc. 28.3 C, 3.6 H and 18.00 CaO). ---  
*b. Trigalacto-tetratartaric acid*  $C^{98}H^{66}O^{70}$ , produced, with elimination of 11 at. water, from 3 at. milk-sugar and 4 at. tartaric acid,  $3C^{12}H^{11}O^{11} + 4C^8H^6O^{12} = 11H_2O$ . Its lime-salt (which reduces potassio-cupric tartrate and yields with nitric acid a large quantity of mucic acid) contains, when dried at  $110^\circ$ , 34.1 p. c. C, 4.5 H and 9.2 lime ( $C^{98}H^{42}Ca^4O^{70} + 10 aq. = 34.6C, 4.4H, 9.5CaO$ ) (Berthelot, *N. Ann. Chim. Phys.* 54, 82; abstr. *Compt. rend.* 45, 268; *J. pr. Chem.* 73, 159; *Chem. Gaz.* 1857, 441). In this Memoir, Berthelot gives for galactoso-tetratartaric acid and its lime-salt, the formulae  $C^{22}H^{16}O^{28}$  and  $C^{22}H^{18}Ca^2O^{28}.4H_2O$ , and for trigalacto-tetratartaric acid and its lime-salt,  $C^{31}H^{20}O^{38}$  and  $C^{31}H^{12}Ca^2O^{38}.2H_2O$ . The formulae above given are from Berthelot's *Chimie organique* 2, 296.

16. Milk-sugar heated in a sealed tube with *aqueous ammonia*, yields a brown nitrogenous product, corresponding to that obtained in like manner from cane-sugar. (P. Thénard, *Bull. Soc. Chim. Paris*, 1861, 42.)

17. Milk-sugar heated with *potassium* or *sodium*, carbonises with faint glow, and converts the metal into alkali. (Gay-Lussac & Thénard.)

18. Crystallised milk-sugar triturated with an equal weight of *potash-hydrate* remains unaltered; but on adding half its weight of water, the mass becomes heated to  $115^\circ$ , and a brown solution is formed, containing carbonic acid, acetic acid, and a brown, somewhat bitter substance, which is insoluble in alcohol and ether, deliquesces in the air, is decolorised by chlorine, and forms precipitates with tin, lead, mercury, and silver salts. (Bouillon & Vogel). — When milk-sugar is heated to  $100^\circ$  with excess of alkali,  $1\frac{1}{2}$  at. alkali is saturated by 1 at. milk-sugar ( $C^{12}$ ). (Dabrunfaut.) When more strongly heated with 4 or 5 pts. hydrate of potash and a small quantity of water, it is decomposed, with evolution of hydrogen and formation of oxalic acid. (Gay-Lussac, *Ann. Chim. Phys.* 41, 398.) Milk-sugar triturated with *potash-hydrate* and water, forms, with rise of temperature, a brown liquid from which alcohol throws down a thick brown syrup, while acetate of lime remains in solution. (See also Combinations, p. 225.)

19. Milk-sugar is not altered by *permanganate of potash*. (Monier, *Compt. rend.* 46, 425; *J. pr. Chem.* 73, 478.)

20. Aqueous milk-sugar mixed with *cupric sulphate* [*hydrate* (Bequerel, *Ann. Chim. Phys.* 47, 17; *Berz. Jahresber.* 12, 321), *chloride* or *acetate* (Baumann)], then with excess of potash-hydrate, yields [if at least 2 at. milk-sugar ( $C^{12}H^{11}O^{11}.H_2O$ ) are present for every 5 at. cupric oxide (Städeler & Krause)], a deep blue, clear solution which, when heated, deposits cuprous oxide (Trommer, *Ann. Pharm.* 39, 360); if the cupric oxide is in excess, the milk-sugar is converted into galactic acid; with an insufficient quantity of cupric oxide, pectolactic acid is likewise formed (Bödeker & Struckmann, *Ann. Pharm.* 100, 264; *J. pr. Chem.* 70, 420.)

*Cupric acetate* and *nitrate* are reduced by milk-sugar at the boiling heat, even without addition of potash (A. Vogel, Buchner); according to Baumann, the acetate is not thus reduced. With the nitrate,

according to A. Vogel & Buchner,—with cupric hydrate and potash according to Becquerel, metallic copper is produced as well as cuprous oxide.—From *cyanide of copper and potassium*, milk-sugar does not separate cuprous oxide (Baumann).

When tartaric acid is added to the solution of cupric sulphate in such proportion that, on supersaturating with potash, the whole remains dissolved, and no cupric or cuprous oxide is separated on boiling (for which, according to Städeler & Krause, 3 at. tartaric acid are required for every 1 at. cupric oxide), then also 8 at. hydrate of potash, milk-sugar does not precipitate any cuprous oxide from the solution at the boiling-heat. If 1 at. more of potash-hydrate be added for each 1 at. cupric oxide, and the solution containing milk-sugar be then heated to  $60^{\circ}$ , the liquid becomes turbid and deposits a yellowish precipitate, which acquires a dingy orange-colour on boiling; it is not till the solution contains 3 at. free alkali to 1 at. cupric oxide that it yields, when heated with milk-sugar, a precipitate of cuprous oxide, which rapidly falls to the bottom (Städeler and Krause).

From these or similarly prepared solutions (see *Glucose*), 1 at. milk-sugar ( $C^{12}H^{14}O^{11},HO$ ) reduces 7 at. cupric oxide (Rigaud, *Ann. Pharm.* 90, 297; Städeler & Krause; Schiff, *Ann. Pharm.* 104, 330). According to earlier determinations by Bodeker (*N. Zeitsch. f. rat. Med.* 6, 201; *Kopp's Jahresber.* 1858, 818), 1 at. milk-sugar reduces 7.5 at. According to his later determinations (*Ann. Pharm.* 100, 264), it reduces  $6\frac{2}{3}$  at. cupric oxide. The quantity of oxide reduced is influenced by the duration of the boiling, and varies between 7.62 and 7.96 at. Hence, for the estimation of milk-sugar, by means of potassio-cupric tartrate, it must be converted into grape-sugar (lactose) (Fehling, *Ann. Pharm.* 104, 79). On the estimation of milk-sugar by means of potassio-cupric tartrate, see also Poggiale (*Comp. rend.* 28, 505; *J. pr. Chem.* 47, 13); Neubauer (*N. Br. Arch.* 72, 277).

21. When aqueous milk-sugar is heated above  $60^{\circ}$  with *oxide of lead*, it becomes brown and empyreumatic. (Berzelius.) — 22. Aqueous milk-sugar boiled with *mercuric oxide* reduces it but partially to mercurous oxide (A. Vogel), but after addition of potash, to metal. (Becquerel.) It does not alter mercurous nitrate (Baumann). — 23. *Nitrate of silver* and *nitrate of argentammonium* are reduced by heating with aqueous milk-sugar; with *bichloride of platinum*, on addition of ammonia, a deep red precipitate is obtained. (Baumann.)

24. Milk-sugar is not brought into the state of vinous fermentation by small quantities of *yeast*, but with larger quantities it ferments, at  $30^{\circ}$ , less quickly than grape-sugar, yielding alcohol and carbonic acid. Yeast does not cause milk-sugar to ferment. (Fourcroy & Vauquelin, *N. Gehl.* 2, 646; Buchholz, *Schw.* 4, 350; Bouillon-Lagrange & Vogel.) In a mixture of milk- and grape-sugar, yeast decomposes the latter, while the milk-sugar remains unaltered. (Berthelot, *N. Ann. Chim. Phys.* 50, 363.) Milk-sugar dissolved in water, together with its own weight of yeast, begins to ferment at  $30^{\circ}$  (Cagniard de Latour, *Inst.* 237, 224); mixed with 18.8 p. c. of its weight of washed upper yeast (*Oberhefe*), it yields between  $12^{\circ}$  and  $25^{\circ}$ , alcohol and saccharic acid. (Schill, *Ann. Pharm.* 31, 132.)

The milk-sugar in whey ferments spontaneously after a while; the fermentation may also be induced by addition of casein, the products being lactic acid, alcohol, and carbonic acid. For details on the lactic fermentation, see *Cane-sugar*, also xi, 478.

Milk likewise ferments spontaneously, and without addition of

yeast, and yields alcohol (Kowsky, *Alm.* 1783, 65; Cagniard de Latour), still more on addition of milk-sugar (Less, *Pogg.* 41, 194; *Ann. Pharm.* 21, 158). Spirit prepared by the spontaneous fermentation of mare's milk in sheep-skin bags, and subsequent distillation, is the *kumis* of the Kalmaucks (comp. G. Rose, *Pogg.* 32, 210). In this fermentation Poggendorff (*Pogg.* 32, 209), Boutron & Fremy (*N. Ann. Chim. Phys.* 2, 257), and others suppose that the formation of the alcohol is preceded by conversion of the milk-sugar into grape-sugar.—The ferment which induces the spontaneous fermentation of milk is likewise found in milk which has been curdled out of contact with the air; when decomposed by heating to  $130^{\circ}$ , it is reproduced on exposing the liquid to the air. (Hoppe.)

Milk-sugar fermented by contact with putrid *casein* or *glutin* at  $15^{\circ}$ – $20^{\circ}$ , yields alcohol. (Schill.) Milk-sugar mixed with cheese and chalk, or with the tissue of the pancreas, yields alcohol and lactic acid, together with a peculiar jelly, but no mannite. (Berthelot.) In the fermentation of whey, whether spontaneous, or induced by yeast, cheese, or a mixture of cheese and chalk, alcohol is obtained as well as lactic acid, but in variable quantity, and less if the acid is neutralised as fast as it is formed. The more dilute the whey, the more does the alcoholic fermentation predominate; it is induced by the remains of the casein, which change to yeast, but soon become inactive. (Luboldt.) In this reaction the milk-sugar is not converted into grape-sugar (or lactose), but exists as milk-sugar in the liquid at all stages of the fermentation. (Berthelot; Luboldt, *J. pr. Chem.* 77, 282.) When milk, after standing for 11 days, is precipitated with a large quantity of alcohol, and the filtrate, after evaporation to a syrup, likewise treated with alcohol, unaltered milk-sugar is precipitated, which could not therefore have been converted by the fermentation into another kind of sugar. (Hoppe, *Arch. pathol. Anat.* 17, 417; abstr. *Kopp's Jahresber.* 1859, 627.) In the solution of milk-sugar, brought into the fermenting state by cheese, yeast, or gluten, Schill formerly found grape-sugar.

Washed calf's rennet in contact with aqueous milk-sugar at  $40^{\circ}$ , forms lactic acid, without evolution of gas (Fremy, *J. Pharm.* 25, 599; *Ann. Pharm.* 31, 188); also the expressed juice of brown cabbage or fresh geranium-leaves, after addition of chalk. (Wackenroder.) White of egg scarcely alters a solution of milk-sugar mixed with chalk, in six weeks, but if coagulated and turned sour under water, it produces lactic acid. (Wackenroder, *N. Br. Arch.* 46, 257.)

25. In contact with Schunck's *erythrozym* (from madder), milk-sugar ferments, producing carbonic acid, hydrogen, alcohol, formic acid, acetic acid, and succinic acid, and generally the same products that are obtained from cane-sugar. (Schunck, *Phil. Mag. J.* [4], 8, 161; *J. pr. Chem.* 63, 222.) For further details see *Cane-sugar*, p. 267.—26. Milk-sugar is not altered by gastric juice. (Hoppe.) On the decompositions in the intestines, blood, and pancreatic juice, see *Handbuch* viii, *Zoochem.* 553 and 589.

*Combinations.* A. *With Water.* a. *Crystallised Milk-sugar.*—Colourless or white crystals belonging to the right prismatic system. Hardness between rock-salt and calcspar. Grates between the teeth. Sp. gr. 1.534 (Schabus); 1.543 at  $13.9^{\circ}$ , (according to Joule & Playfair). Its taste is slightly sweet and rather sandy. Dextro-rotatory

power  $[\alpha]_j = 56.4^\circ$ , vid. inf. p. 245. For the expansion, according to Playfair & Joule, see *Chem. Soc. Qu. J.* 1, 121; *Lieb. Kopp. Jahresber.* 1847—1848, p. 57.

The crystals are hemihedral and hemimorphous. Of the rhombic octahedron, *a* (fig. 41), the upper half is altogether wanting; of the lower half, only the face *a''* and its opposite to the right behind are present, together with the pairs of faces *t* and *m* (fig. 53) and the horizontal face *ii* from figure 52. In these latter, the faces of the upper half are more strongly developed than those of the lower half, whereas with the *t*-faces, the contrary is the case. The face *t* is mostly curved, and in the larger crystals, striated parallel to the combination-edge with *ii*, which latter is also striated parallel to its combination-edge with *m*; hence the measurements are only approximate;  $\alpha : a$  over  $t = 23^\circ 22'$ ;  $\alpha : m = 109^\circ 1'$ ;  $\alpha : t = 101^\circ 41'$ ;  $ii : ii$  over  $t = 39^\circ 18'$  obs.,  $38^\circ 6'$  calc.;  $ii : t = 109^\circ 39'$ ;  $ii : m = 160^\circ 21'$  obs.;  $160^\circ 57'$  calc. The differences between these angular data and those given by Rammelsberg, arise from Rammelsberg having used somewhat different parameters for the faces *ii*. — Cleavage parallel to *m*. The faces *t*, *ii*, and *m*, have in the larger crystals, a splendid mother-of-pearl lustre, which, in the smaller crystals, inclines strongly to vitreous;  $\alpha$  with unctuous or mother-of-pearl lustre. (Schabus, *Bestimmung*, 49; *Rammelsberg's Nachtrag*, 219.)\*

Permanent at mean temperatures and at  $100^\circ$ ; gives off its water slowly at  $130^\circ$ , more quickly between  $140^\circ$  and  $145^\circ$ , amounting on the average to 5.08 p. c. (1 at. = 5.00 p. c.) and is converted into anhydrous milk-sugar.

At mean temperature or at $100^\circ$ .				Liebig.	Berzelius.
12 C .....	72	...	40.00	39.36	38.73
12 H .....	12	...	6.66	6.67	7.16
12 O .....	96	...	53.34	53.97	54.11
$C^{12}H^{11}O^{11}, HO$ .....				100.00	100.00

Gay-Lussac & Thénard.	Berthollet.	Prout.	Städeler & Krause.		Dubrunfaut.
			<i>a.</i>	<i>b.</i>	
C 38.02 .....	41.13	39.15	39.68	40.07	39.70
H 7.34 .....	6.76	6.67	6.77	6.70	6.67
O 54.64 .....	52.11	54.18	53.55	53.23	53.63
100.00 .....	100.00	100.00	100.00	100.00	100.00

*a.* Air-dried; *b.* dried at  $100^\circ$  (Städeler & Krause).

*b. Aqueous Milk-sugar.*—Crystallised milk-sugar is slightly hygroscopic. It dissolves in 5 or 6 pts. of cold and in 2.5 pts. boiling water; according to Guérin-Varry, in 9 pts. water at  $20^\circ$ , and in 1 part boiling water. The saturated solution produced by prolonged contact of water with excess of milk-sugar at  $10^\circ$ , has a density of 1.055 and contains 14.55 p. c. of crystallised milk-sugar. When left to evapo-

\* The formula of the crystals, according to Naumann's notation, is  $\infty \check{P} \infty \cdot \frac{P}{4}$   
 $\infty P \cdot 2\check{P} \infty$ . Inclination of  $\infty P : 2\check{P} \infty = 109^\circ 39'$ ;  $\infty P : \frac{P}{4} = 101^\circ 41'$ . Ratio of  
 axes,  $a : b : c = 0.6215 : 1 : 0.2193$ . (Schabus.)

rate, it begins to deposit crystals as soon as it attains the density of 1.063 and contains 21.64 p. c. milk-sugar. (Dubrunfaut.) When milk-sugar dissolves, heat is evolved, according to Dubrunfaut; according to Pohl (*J. pr. Chem.* 82, 154), 175.2 grm. milk-sugar dissolved in 1.051 kilogs. water at 16.5 lowers the temperature to 15.62°. — The dextro-rotatory power of a recently prepared aqueous solution of milk-sugar is greater in the ratio of 8 to 5 than that of the same solution after standing for some time or after being heated. The rotatory power diminishes slowly at 0°, more quickly on heating, and in two minutes at the boiling heat, to that of  $[\alpha]_D^{20} = 56.4'$  for crystallised milk-sugar. (E. O. Erdmann, *Lieb. Kopp. Jahresber.* 1855, 671; Dubrunfaut.) A warm saturated solution of milk-sugar, kept for 10 minutes in a sealed tube crystallises when the tube is opened, and partially when the temperature is raised from  $-10$  to  $+18^\circ$ . (Lieben.)

B. *With Acids.* — Pulverized milk-sugar absorbs *hydrochloric acid gas* turning slightly grey, and if oil of vitriol is afterwards poured upon it gives off hydrochloric acid with violent effervescence. Aqueous hydrochloric acid dissolves milk-sugar more freely than pure water. (Bouillon & Vogel.)

C. *With Bases.* Milk-sugar unites with bases, giving off water at the same time (Berzelius, Brendecke). With aqueous alkalis or alkaline earths, if the temperature be kept low and the action not too long continued, compounds of milk-sugar may be formed which have less rotatory power than the milk-sugar contained in them, yield unaltered milk-sugar when decomposed, and contain 3 at. potash or soda to 1 at. milk-sugar,  $C^{12}H^{11}O^{11}$  (Dubrunfaut, *vid. inf.*).

Milk-sugar absorbs 12.4 per cent. *ammonia-gas*, of which 5.8 per cent. volatilises after exposure to the air for two hours, the rest remaining more intimately combined (Berzelius).

*Potassium-compound.* — The solution of 1 pt. potash-hydrate in 3 pts. water dissolves 7 pts. of milk-sugar, and yields a precipitate with alcohol after dilution with a small quantity of water. The flocculent, strongly alkaline precipitate, easily soluble in water, is decomposed by carbonic and other acids, with separation of milk-sugar. (Brendecke.)

*Sodium-compound.* — The solution of 1 pt. soda-hydrate in 3 pts. water dissolves from 20 to 21 pts. milk-sugar and is then precipitable by alcohol (Brendecke).

					Brendecke.
NaO .....	31	.....	8.12	.....	8.3
$C^{12}H^{11}O^{11}$ .....	351	.....	91.88	.....	
<hr/>					
$C^{12}H^{11}O^{11}, NaO, HO$ .....	382	.....	100.00	.....	

Milk-sugar does not unite with *common salt* (Stadeler & Krause).

*Barium-compound.* — Milk-sugar is triturated with baryta-water, and the filtrate precipitated with alcohol. Contains 40.00 per cent. baryta, and is therefore  $C^{12}H^{11}O^{11}, 2BaO$  (calc. 40.15 BaO) (Brendecke).

*Calcium-compound.* — Milk-sugar forms, with lime, a soluble compound containing equal numbers of atoms of lime and milk-sugar ( $C^{12}H^{11}O^{11}$ ) and an insoluble basic compound which is obtained by treating milk-sugar with a large quantity of dry hydrate of lime (Dubrunfaut).

When aqueous milk-sugar is added to milk of lime till the latter is nearly dissolved, alcohol throws down from the filtrate a precipitate containing 15.7 per cent. lime (Brendecke.) The solution of lime in milk-sugar deposits, on exposure to the air, crystals of quinto-hydrated carbonate of lime (Pelouze, *Ann. Chim. Phys.* 48, 307).

*Lead-compound.*—When milk-sugar is digested with oxide of lead and water at 50°, a soluble compound is obtained, together with another suspended in the liquid. The latter, obtained by filtration in air free from carbonic acid, is gummy, becomes grey and translucent when dry, turns yellow and gives off water at 100°, and then contains 63.52 per cent. PbO. The solution, which has a sweet, alkaline, astringent taste, leaves, when evaporated in vacuo, a yellow gum soluble in water, and containing 18.12 per cent. PbO. From its solution, ammonia precipitates the insoluble compound (Berzelius, *Lehrb.* 3 Aufl. 9, 690). Dubrunfaut doubts whether these compounds still contain unaltered milk-sugar.

Milk-sugar hinders the precipitation of *ferric salts* by alkalis. (H. Rose.) On the compound with cupric oxide, *vid. sup.*

Milk-sugar dissolves readily in *distilled vinegar*, and crystallises unaltered on evaporation (Bouillon & Vogel).

Milk-sugar is insoluble in *alcohol* and *ether*.

### Appendix to Milk-sugar.

#### 1. Lactose.



PASTEUR (1856). *Compt. rend.* 42, 347; *Inst.* 1856, 91; *J. pr. Chem.* 68, 427; *Chem. Centr.* 1856, 253.

*Gallactose* (Berthelot), *Mucoglucose*.—According to Berthelot, Bouchardat was the first to distinguish lactose from grape-sugar. — Lactose is perhaps identical with the sugar produced by boiling gum with dilute acids (p. 199). (Berthelot, *Chim. org.* 2, 249). — E. O. Erdmann (*Lieb. Kopp. Jahresber.* 1855, 672) likewise recognised the peculiar properties of lactose before Pasteur.

Milk-sugar is boiled for several hours with 4 pts. of water and 2 per. cent. oil of vitriol, the liquid neutralised with chalk, the filtrate evaporated to a syrup, and then left to crystallise.

Lactose crystallises more readily than grape-sugar, in nodules consisting of microscopic, limpid, rectangular prisms acuminate at the ends,—more generally of six-sided, round-edged laminæ having a pea-shaped protuberance in the middle. Dextro-rotatory power  $[\alpha]_D^{20} = 83.22^\circ$  at 15°; in the recently-prepared solution it is stronger  $[\alpha]_D^{20} = 139.66^\circ$ , but sinks to the former magnitude slowly at ordinary temperatures; instantly on boiling.

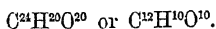
Lactose yields with *nitric acid* twice as much mucic acid as milk-sugar. — From an alkaline solution it reduces as much *cupric oxide* as grape-sugar. — It ferments in contact with *yeast*. If the fermentation



be interrupted before it is complete, the liquid still contains unaltered lactose, which therefore has not undergone any division or further alteration during the fermentation. In this fermentation, the same products are formed as in the fermentation of cane-sugar. (Pasteur, *N. Ann. Chim. Phys.* 58, 356.)

Lactose dissolves in *water*. It does not combine with *chloride of sodium*, and dissolves but very sparingly in cold *alcohol*.

## 2. Lactocaramel.



A. LIEBEN. (1856.) *Wien. Akad. Ber.* 18, 180; *J. pr. Chem.* 68, 407; *Chem. Centr.* 1856, 548.

*Anhydrous Milk-sugar* (Berzelius, *Lehrb.* 3 Aufl. 9, 690).

Formed, together with variable quantities of anhydrous milk-sugar and a substance insoluble in water, by heating milk-sugar to between  $170^{\circ}$  and  $180^{\circ}$ .

Milk-sugar is heated for several hours to  $180^{\circ}$ ; the pulverised residue is exhausted with boiling alcohol; the insoluble portion which has deliquesced to a syrup, is dissolved in water; and the filtrate is evaporated.

Dark brown, brittle, shining mass, becoming, after trituration, of a lighter brown than caramel.

	at $100^{\circ}$ .				Lieben.
24 C.....	144	.....	44.44	.....	44.36
20 H .....	20	.....	6.17	.....	6.26
20 O .....	160	.....	49.39	.....	49.38
<hr/>					
$C^{24}H^{20}O^{20}$ .....	324	.....	100.00	.....	100.00

Lacto-caramel is converted by heat into a substance insoluble in water, gradually at  $170^{\circ}$ , more quickly at temperatures above  $200^{\circ}$ . This insoluble substance is likewise produced in the preparation of lacto-caramel. It dissolves in nitric acid, partially in potash-ley, and is precipitated therefrom as red-brown powder by hydrochloric acid. It is quickly decomposed by dilute *sulphuric acid* and *bichromate of potash*, with formation of chromic oxide.

Lacto-caramel dissolves readily in *water* and is precipitated as a brown gum by alcohol.

Aqueous lacto-caramel does not precipitate baryta-water.

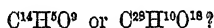
*Lead-compound.* — Aqueous lacto-caramel precipitates from ammoniacal sugar of lead a coffee-coloured powder, which when treated with cupric acetate forms the copper-compound of lacto-caramel. It dissolves readily in acids, but is insoluble in water and in alcohol.

*Copper-compound.* — Aqueous protochloride of copper is mixed in the cold with a large excess of concentrated soda-ley, and the mixture is precipitated with aqueous lacto-caramel. — The compound is also produced when aqueous cupric acetate is poured upon the lead-com-

pound of lacto-caramel. — Olive-green powder which gives off 3.55 p. c. water at 100°, and 7.85 p. c. at 150°, acquiring a darker colour, and blackening at a higher temperature. — It is nearly insoluble in water. By boiling it for some time with water, a solution is obtained, which does not yield the compound by evaporation, but on addition of alcohol deposits green flocks, easily soluble in water.

	<i>In vacuo.</i>		Lieben.	
24 C .....	144.0	34.17	34.26	
22 H .....	22.0	5.22	5.19	
22 O .....	176.0	41.77	42.68	
2 CuO .....	79.4	18.84	17.87	
$C^{24}H^{22}Cu^2O^{24}$ .....	421.4	100.00	100.00	
	<i>at 150°.</i>		Lieben.	
24 C .....	144.0	37.36	36.74	
18 H .....	18.0	4.67	4.69	
18 O .....	144.0	37.37	38.79	
2 CuO .....	79.4	20.60	19.78	
$C^{24}H^{18}Cu^2O^{20}$ .....	385.4	100.00	100.00	

### 3. Gallactic Acid.



BÖDEKER & STRUCKMANN. *Ann. Pharm.* 100, 264; *J. pr. Chem.* 70, 414.

Produced when milk-sugar is oxidised by cupric oxide in an alkaline solution.

200 grm. milk-sugar are dissolved, together with 1200 grm. cupric sulphate in warm water; soda-ley is added till the precipitate at first produced is redissolved; the liquid is heated to boiling and filtered from the precipitated cuprous and cupric oxides; and the filtrate is evaporated till as much as possible of the sulphate of soda has been removed by crystallisation. The mother-liquor is precipitated with acetate of baryta, freed from humoid substances by the addition of a small quantity of neutral acetate of lead, and after filtering, mixed with excess of that salt, whereby gallactate of lead is precipitated,—whereas, if the quantity of cupric sulphate added is insufficient for complete oxidation, pectolactic acid (p. 231) remains in solution and may be precipitated by basic acetate of lead. From the washed gallactate of lead, the acid may be separated by decomposing the salt with hydrosulphuric acid under water, evaporating the filtrate, redissolving in alcohol, and again evaporating. If the product is still contaminated with residues of soda, baryta, or pectolactic acid, it must be reprecipitated with neutral acetate of lead, and the precipitate decomposed as above.

Pale yellow, inodorous, strongly acid syrup.

Heated on platinum-foil, it smells like burning malic acid, takes fire and leaves a residue of charcoal. — Not altered by *potassio-cupric tartrate*.

Soluble in all proportions in *water*.

With bases it forms the *gallactates*. These salts, according to Bödeker & Struckmann, are bibasic,  $C^{14}H^3M^2O^9$ , amorphous and mostly deliquescent.

The aqueous acid does not precipitate: baryta-water, the hydrochlorates of lime, baryta, zinc-oxide, ferric oxide and mercuric oxide, or cupric sulphate, or nitrate of silver; but from *ferric acetate*, it throws down a red-brown, and from *mercurous* or *mercuric nitrate*, a white precipitate.

The *Gallactates of Ammonia, Potash, Soda and Baryta* are deliquescent; they remain, when their aqueous solutions are evaporated, as amber-yellow amorphous masses, and are precipitated from their aqueous solutions by alcohol, in white flocks which deliquesce on standing.

*Gallactate of Lime*.—Aqueous gallactic acid is digested with pounded marble or neutralised with milk of lime, and the filtered solutions are precipitated with excess of lime-water. — White flocks, forming when dry, a pale yellow powder. Dried over oil of vitriol, it contains 24.5 p. c. lime ( $C^{14}H^3O^7, 2CaO + 3aq. = 24.78$  p. c.  $CaO$ ), gives off 13.28 p. c. water at  $110^\circ$  (calc. 11.95), and then contains 28.26 p. c.  $CaO$  ( $C^{14}H^3O^7, 2CaO = 28.14$  p. c.).

*Gallactate of Lead*. — Heavy white powder.

Over oil of vitriol.				Bödeker & Struckmann.	
14 C .....	84.0	...	19.98	.....	19.83
9 H .....	9.0	...	2.14	.....	2.11
13 O .....	104.0	...	24.74	.....	24.11
2 PbO .....	223.4	...	53.14	.....	53.95
$C^{14}H^3O^7, 2PbO + 6aq. ....$				420.4	100.00
				100.00	100.00
at $120^\circ$ .				Bödeker & Struckmann.	
14 C .....	84.0	...	21.35	.....	21.22
6 H .....	6.0	...	1.53	.....	1.48
10 O .....	80.0	...	20.33	.....	19.58
2 PbO .....	223.4	...	56.79	.....	57.72
$C^{14}H^3O^7, 2PbO + 3aq. ....$				393.4	100.00
				100.00	100.00

So according to Bödeker & Struckmann.

*Gallactate of Copper*.—Obtained by double decomposition as a light-blue gummy precipitate.

*Mercurous Gallactate*.—From mercurous nitrate and the aqueous acid. Dissolves with difficulty in dilute nitric acid.

*Mercuric Gallactate*.—Precipitated from the aqueous acid by mercuric nitrate, as a white amorphous body, pale yellow when dry. After drying over oil of vitriol, it contains 55.03 p. c.  $HgO$ , gives off 7.92 p. c. water at  $110^\circ$ , and then contains 59.77 p. c. mercuric oxide ( $C^{14}H^3O^7, 2HgO + 3aq. = 55.96$  p. c.  $HgO$ , 7.00  $H_2O$ , and 60.17 p. c.  $HgO$  in the dried salt).

Gallactic acid dissolves in *alcohol*, but not in *ether*.

## 4. Pectolactic Acid.



BÖDEKER & STRUCKMANN. *Ann. Pharm.* 100, 264, abstr. *J. pr. Chem.* 70, 414.

Obtained in the preparation of gallactic acid, especially when the milk-sugar is heated with an insufficient quantity of free alkali, and less cupric oxide than is sufficient to convert it completely into gallactic acid. Remains in solution after the gallactic acid has been precipitated with neutral acetate of lead, is precipitated by basic acetate of lead, and obtained in the free state by decomposing the washed precipitate with sulphuretted hydrogen, as described for gallactic acid (p. 229).

Scentless, brown, acid syrup. After drying over oil of vitriol it retains 5 at. water, at 100°, 2 at.

Over oil of vitriol.				Bödeker & Struckmann.	
16 C .....	96	...	39.18	.....	39.10
13 H .....	13	...	5.31	.....	6.10
17 O .....	136	...	55.51	.....	54.80
$\text{C}^{16}\text{H}^8\text{O}^{12} + 5\text{aq.}$ .....	245	...	100.00	.....	100.00

at 120°.				Bödeker & Struckmann.	
16 C .....	96	...	44.04	.....	43.48
10 H .....	10	...	4.59	.....	5.48
14 O .....	112	...	51.37	.....	51.04
$\text{C}^{16}\text{H}^8\text{O}^{12} + 2\text{aq.}$ .....	218	...	100.00	.....	100.00

From *potassio-cupric tartrate*, at the boiling heat, it reduces cuprous oxide. — It does not alter aqueous *nitrate of silver* in the cold, but colours it yellow on boiling; purple-red after addition of ammonia and precipitates the metal in the specular form. May not the acid have contained milk-sugar? Kr.

The *pectolactates*, according to Bödeker & Struckmann, are *bibasic*  $\text{C}^{16}\text{H}^6\text{M}^2\text{O}^{12}$ ; those of the alkalis and alkaline earths are easily soluble in water, but with exception of the lime-salt, precipitable by alcohol. The only pectolactate that has been obtained in the anhydrous state is the basic ferric salt.

*Pectolactate of Baryta.* — Obtained by neutralising the acid with baryta-water, and precipitating with alcohol, as a sticky mass, changing to a white powder when absolute alcohol is poured upon it. After drying over oil of vitriol, it gives off 5.75 p. c. water at 100°. Dried over oil of vitriol it contains, on the average, 21.77 p. c. C., 3.61 H., and 36.89 BaO; after drying at 100°, it contains 23.00 C., 3.00 H., and 39.08 BaO. Bödeker & Struckmann assign to the former salt the formula  $\text{C}^{16}\text{H}^6\text{O}^{10}, 2\text{BaO} + 9\text{aq.}$ , to the latter,  $\text{C}^{16}\text{H}^6\text{O}^{10}, 2\text{BaO} + 6\text{aq.}$  Calculation agrees with the analytical results so far as regards the baryta and hydrogen, but not for the carbon, because, according to B. & St., a portion of the latter remained unburned.

*Ferric Pectolactate.* — Obtained by precipitating ferric acetate with

pectolactate of ammonia, as a rust-coloured precipitate soluble in soda-ley. — *a. Dried over oil of vitriol.* Contains 60·8 p. c.  $Fe^2O^3$ , gives off 15·48 p. c. water at  $120^\circ$ , and is therefore  $C^{16}H^6O^{10}, 6Fe^2O^3 + 14aq.$  (calc. 60·91  $Fe^2O^3$ , 15·81 aq.) — *b. Dried at  $100^\circ$ .* Contains 65·41 p. c.  $Fe^2O^3$ , gives off 9·1 p. c. water at  $120^\circ$ , and is therefore  $C^{16}H^6O^{10}, 6Fe^2O^3 + 8aq.$  (calc. 65·39  $Fe^2O^3$  and 9·81 aq.). — *c. At  $120^\circ$ .* Contains from 71·4 to 72·4 p. c.  $Fe^2O^3$ , and is therefore  $C^{18}H^6O^{10}, 6Fe^2O^3$  (calc. 72·51  $Fe^2O^3$ ) Bødeker & Struckmann.

Pectolactic acid is soluble in *alcohol*, insoluble in *ether*.

## ¶ 5. Isobiglycolethylenic Acid.



HLASIWETZ (1861) *Ann. Pharm.* 119, 281.

BARTH & HLASIWETZ. *Ann. Pharm.* 122, 96.

### *Isodigycoläthylensäure.*

*Formation.* By treating milk-sugar or gum-arabic with bromine, and decomposing the resulting brominated compound with moist oxide of silver or of lead, or with caustic soda. The composition of the brominated product has not been exactly ascertained. Barth & Hlasiwetz however suppose that it has the composition  $C^{12}H^{10}O^{10}Br^2$  and is formed from milk-sugar by the simple addition of 2 at. bromine [and elimination of 1 at. water]. The formation of isobiglycolethylenic acid from it by the action of bases may then be supposed to take place as represented by the equation:  $C^{12}H^{10}O^{10}Br^2 + 2AgO = C^{12}H^{10}O^{12} + 2AgBr$ . They find, in fact, that 2 at. bromine are sufficient for the production of this compound from 1 at. milk-sugar, though in their earlier experiments they used 4 at. bromine, supposing that a substitution-product would be formed ( $C^{12}H^{11}O^{11} + Br^4 = C^{12}H^8Br^2O^{10} + 2HBr + HO$ ). Hydrobromic acid is, in fact, produced as well as carbonic acid and other products; but these appear to result from a secondary action, and are formed more abundantly as the proportion of bromine used is larger. Moreover the decomposition of the compound  $C^{12}H^8Br^2O^{10}$  by oxide of silver, &c., would yield, not  $C^{12}H^{10}O^{12}$ , but  $C^{12}H^8O^{12}$ .

*Preparation.* 1. The milk-sugar, or gum, and bromine, together with a convenient quantity of water, are enclosed, according to the quantity of material used, either in sealed tubes or in strong glass bottles (champagne or soda-water bottles) secured with caoutchouc stoppers and binding wire, and heated in the water-bath for five or six hours till the bromine disappears, and a colourless or yellowish liquid is produced. The tubes or bottles are then opened, whereupon carbonic acid escapes and an odour like that of chloroform becomes perceptible; the somewhat dilute liquid is neutralised with moist oxide of silver or oxide of lead; the pasty mass is washed on a filter with hot water; and the filtrate—which, when oxide of silver is used, soon becomes coloured by reduced silver—is precipitated with hydro-sulphuric acid. If the filtered liquid be then merely freed from hydro-sulphuric acid by heat and concentrated, it does not yield the acid in crystals, as it is still somewhat impure. To purify it further, it is evaporated to a small bulk at a gentle heat; freed from lime (which is always present in commercial milk-sugar) by adding alcohol as long

as turbidity is thereby produced; then filtered; distilled to remove the alcohol; diluted; boiled to drive off the last portions of alcohol; treated, while still hot, with carbonate of cadmium till it ceases to effervesce; and the solution of the cadmium-salt, which has a slight acid reaction, is decolorised with animal charcoal and left to crystallise, an additional quantity being obtained from the mother-liquors. This salt is but sparingly soluble even in boiling water; the cadmium may, however, be easily separated from it by passing sulphuretted hydrogen into a thin paste of the salt, kept at the boiling heat in a flask, the acid thus gradually set free dissolving the rest of the salt. Finally, the liquid filtered from sulphide of cadmium is concentrated over the water-bath to a thin syrup and left to crystallise; it then, after a few days, yields groups of crystalline needles, and the whole gradually solidifies to a soft crystalline mass, which becomes friable when dried over oil of vitriol in vacuo.

2. The liquid obtained as above by heating milk-sugar or gum with bromine is saturated with soda and boiled; whereby it acquires an acid reaction. If again neutralised, concentrated, and left to stand, it deposits a mixture of crystals, which must be freed from the mother-liquor by pressure and redissolved. Isobiglycolethylenate of sodium then crystallises out alone, and may be purified by animal charcoal. It may be converted into the cadmium-salt by precipitation, and the acid obtained therefrom as above.

*Properties.* Small, highly deliquescent needles. Taste sour and agreeable, much weakened by dilution with water. Melts to a syrup at the heat of the water-bath. Lævo-rotatory. A solution, 72 mm. long and containing 11·137 p. c. of the acid, produces a deflection of 2° to the left.

	<i>Dried at 100°.</i>		<i>Barth &amp; Hlasiwetz.</i>	
			<i>from Milk-sugar.</i>	<i>from Gum-arabic.</i>
			<i>(mean.)</i>	
12 C.....	72	40·45	40·37	40·28
10 H.....	10	5·61	5·85	5·69
12 O.....	96	53·94	53·78	54·03
$C^{12}H^{10}O^{12}$ .....	178	100·00	100·00	100·00

It is isomeric with Wurtz's *biglycolethylenic acid*;—may be derived from milk-sugar,  $C^{12}H^{11}O^{11}$  by abstraction of 1 at. water and addition of 2 at. oxygen; differs from tartaric acid,  $C^8H^6O^{12}$ , by  $2C^2H^2$ , from aconitic acid,  $C^{12}H^6O^{12}$ , by  $H^4$ , and from Goup's mannitic acid,  $C^{12}H^{12}O^{14}$ , by 2 HO.

*Decompositions.* 1. The acid becomes somewhat coloured when heated for some time to 100°. Heated on platinum-foil, it burns with an odour of sugar and formation of a tumefied perfectly combustible coal.—2. When carefully oxidised with *nitric acid*, it yields chiefly mucic acid.—3. Fused with *potash*, it yields acetic and oxalic acids, together with other products.—4. The aqueous solution neutralised with ammonia reduces *nitrate of silver* when heated, forming a specular deposit of silver.—5. It reduces an alkaline solution of *cupric oxide*, when heated with it.

*Combinations.* A. *With Water.* The acid dried over oil of vitriol

in vacuo, gives off, when heated to  $100^{\circ}$  for 24 hours, 13.9 p. c. water, corresponding to the formula  $C^{12}H^{10}O^{12} + 3HO$  (calc. 13.19 p. c.) A sample heated for 12 hours only, gave by analysis 38.2 p. c. carbon, and 6.02 hydrogen, corresponding to the formula  $C^{12}H^{10}O^{12} + HO$ .

The acid dissolves easily in water.

**B. With Bases.** All the salts of isobiglycoethylenic acid hitherto obtained, except the lead-salt, agree with the formula  $C^{12}H^8MO^{12}$ . The acid appears therefore (if it contains only 12 at. O.) to be monobasic, though, in its mode of formation and its reactions with nitric acid and with potash, it appears rather to resemble the polybasic acids. Most of its salts dissolve easily in water and crystallise well; the cadmium and silver salts however are but sparingly soluble. They are insoluble in alcohol, which precipitates them from their aqueous solutions. They contain water of crystallisation, which they do not give off completely till heated to  $140^{\circ}$ , and even then not without partial decomposition.

The aqueous solution of the acid is not precipitated by baryta- or lime-water, by acetate of lead, either neutral or basic, or by mercuric nitrate; but *acetate of lead* mixed with ammonia precipitates it completely. It easily dissolves hydrated *cupric oxide*; does not alter ferric chloride.

**Ammonia-salt.** — On mixing the aqueous acid with excess of ammonia, boiling till the odour of ammonia is no longer perceptible, decolorising with charcoal, and concentrating to a thickish consistence, the ammonia-salt separates after a few days in crystals, which may be purified by recrystallisation. When prepared from a sufficient quantity of material, it forms thick, solid, transparent, colourless crystals belonging to the oblique prismatic system, sometimes 4 or 5 mm. broad, easily soluble in water, nearly insoluble in alcohol.

<i>Air-dried.</i>				Barth & Hlasiwetz. <i>mean.</i>	
12 C .....	72	...	33.80	.....	33.69
15 H .....	15	...	7.03	.....	7.37
N .....	14	...	6.52	.....	6.64
14 O .....	112	...	52.65	.....	52.30
$C^{12}H^8(NH^4)O^{12} + 2aq.$ .....				213	...
				100.00	..... 100.00

Heated for some time to  $100^{\circ}$ , it gives off 3.68 p. c. (nearly 1 at.) water, and at  $120^{\circ}$ , at which temperature however it becomes slightly brown, 8.74 p. c. (calc. 2 at. = 8.44 p. c.).

**Potash-salt.** — Extremely soluble in water, and not obtainable in the crystalline form. An alcoholic solution of the acid mixed with alcoholic potash yields the salt in the form of a clotted precipitate which becomes brittle and friable when dried at  $100^{\circ}$ .

**Soda-salt.** — Prepared as already described (p. 233), or by neutralising the aqueous acid with carbonate of soda. Crystallises readily in tufts of small colourless prisms containing 6 at. water, of which 4 at. or 14.45 p. c. (calc. 14.17 p. c.) are given off at  $100^{\circ}$ .

<i>at 100°.</i>				Barth & Hlasiwetz.	
				<i>a.</i>	<i>b.</i>
12 C .....	72	...	33·03	...	33·43
11 H .....	11	...	5·05	...	5·35
Na .....	23	...	10·55	...	10·30
14 O .....	112	...	51·37	...	50·92

$\text{C}^{12}\text{H}^9\text{NaO}^{12} + 2\text{aq.}$  ..... 218 .... 100·00 ... 100·00

<i>Air-dried.</i>				Barth & Hlasiwetz.	
				<i>a.</i>	<i>b.</i>
$\text{C}^{12}\text{H}^{11}\text{NaO}^{14}$ .....	218	...	85·83	...	...
4 HO .....	36	...	14·17	...	14·45

$\text{C}^{12}\text{H}^9\text{NaO}^{12} + 6\text{aq.}$  ..... 254 .... 100·00

*a.* Prepared by neutralising the aqueous acid with carbonate of soda; *b.* by decomposing the brominated acid (p. 233) with caustic soda.

*Baryta-salt.*—The solution of the acid saturated with caustic baryta or the carbonate dries up to a gummy mass.

*Strontia-salt.*—Resembles the baryta-salt.

*Lime-salt.*—From a boiling aqueous solution of the acid, either pure or crude, neutralised with carbonate of lime and decolorised with charcoal, the lime-salt separates in crystals often united in crusts, and tightly attached to the sides of the vessel. By recrystallisation from more dilute solutions it is obtained in rather large, thick, perfectly colourless shining tables.—The crystals contain 7 at. water, 4 of which are given off at 100° and the rest at 140°.

<i>at 140°.</i>				Barth & Hlasiwetz.	
12 C .....	72	.....	36·54	.....	35·63
9 H .....	9	.....	4·57	.....	5·11
Ca .....	20	.....	10·15	.....	10·31
12 O .....	96	.....	48·74	.....	48·95

$\text{C}^{12}\text{H}^9\text{CaO}^{12}$  ..... 197 ..... 100·00 ..... 100·00

<i>at 100°.</i>				Barth & Hlasiwetz.	
				<i>mean.</i>	
12 C .....	72	.....	32·14	.....	31·79
12 H .....	12	.....	5·35	.....	5·65
Ca .....	20	.....	8·92	.....	8·65
15 O .....	120	.....	53·59	.....	53·91

$\text{C}^{12}\text{H}^9\text{CaO}^{12} + 3\text{aq.}$  .... 224 ..... 100·00 ..... 100·00

<i>Air-dried.</i>				Barth & Hlasiwetz.	
				<i>mean.</i>	
12 C .....	72	...	27·69	...	27·69
16 H .....	16	...	6·15	...	6·41
Ca .....	20	...	7·69	...	7·77
19 O .....	152	...	58·47	...	58·13

$\text{C}^{12}\text{H}^9\text{CaO}^{12} + 7\text{aq.}$  ..... 260 .... 100·00 ... 100·00

Or :				Barth & Hlasiwetz.	
$\text{C}^{12}\text{H}^9\text{CaO}^{12}$ .....	197	...	75·68	...	...
7 HO .....	63	...	24·32	...	25·41

$\text{C}^{12}\text{H}^9\text{CaO}^{12} + 7\text{aq.}$  ..... 260 .... 100·00



The quantity of water given off at  $100^\circ$  was in two experiments 13.63 and 13.42 p. c.; calculation for 4 at. gives 13.81 p. c.

Another hydrate containing  $3\frac{1}{2}$  at. water was obtained from the strongly coloured syrupy mother-liquid which remained after the preparation of the lime-salt by treating the crude acid with carbonate of lime. The colouring matter was removed by precipitation with acetate of lead; the filtered liquid was treated with hydro-sulphuric acid; concentrated; precipitated with alcohol; and the viscid lime-salt thus obtained was redissolved in water, decolorised with animal charcoal, and crystallised. It was thus obtained in small crystals which filled the liquid and reduced it to a pasty mass.

<i>Air-dried.</i>			Barth & Hlasiwetz.		
24 C .....	144	...	31.51 .....	31.39	
25 H .....	25	...	5.47 .....	5.66	
2 Ca .....	40	...	8.75 .....	8.81	
31 O .....	248	...	54.27 .....	54.14	
$2C^{12}H^9CaO^{12} + 7aq.$			457	100.00	100.00

*Cadmium-salt.* (Preparation p. 233). The salt crystallises with different quantities of water, according to the concentration of the solution from which it separates.

*a.*  $C^{12}H^9CdO^{12} + 3HO$ . Separates during the cooling of hot saturated solutions, in small crystals united in friable aggregates, and presenting under the microscope the appearance of oblique prismatic (monoclinic) needles, very much flattened by the predominance of the faces parallel to the clinodiagonal. They give off 10.12 p. c. water (3 at. = 10.38) p. c. at  $140^\circ$ , but do not become completely anhydrous till heated to  $150^\circ$  in a current of air, and at the same time become somewhat coloured. Very slightly soluble in water, even at the boiling heat.

<i>Air-dried.</i>			Barth & Hlasiwetz.		
			<i>a.</i>	<i>β.</i>	<i>γ.</i>
12 C.....	72	27.69	27.49	27.73	27.78
12 H .....	12	4.61	4.89	4.92	4.83
Cd .....	56	21.53	21.36	20.87	
15 O .....	120	46.17	46.26	46.48	
$C^{12}H^9CdO + 3aq.$			260	100.00	100.00

*a.* Mean of six analyses of the salt prepared, as described at page 232, from isobiglycoethylenic acid obtained by heating 1 at. milk-sugar with 4 at. bromine, decomposing the product with oxide of silver, &c.—*β.* Analysis of the salt prepared with acid obtained from 1 at. milk-sugar and 2 at. bromine.—*γ.* The same with 8 at. bromine.

*b.*  $C^{12}H^9CdO^{12} + 6HO$ . Separates by slow evaporation from the mother-liquor of the preceding, or generally from dilute solutions, by spontaneous evaporation, in well developed, shining, monoclinic crystals, mostly united in tufts. Very sparingly soluble in cold water; rather more soluble than the preceding in boiling water.

				Barth & Hlasiwetz.	
				<i>a.</i>	<i>β.</i>
<i>Air-dried.</i>				<i>mean.</i>	<i>mean.</i>
12 C .....	72	....	25.08	24.77	25.19
15 H .....	15	....	5.22	5.50	5.53
Cd .....	56	....	19.50	19.25	19.02
18 O .....	144	....	50.20	50.48	50.26
$C^{12}H^9CdO^{12} + 6 aq.$ .....				287	100.00
				100.00	100.00

*α.* Prepared from milk-sugar. — *β.* Prepared from gum-arabic.

This hydrate, like the preceding, cannot be completely dehydrated without slight coloration. At  $140^{\circ}$  it lost, in two experiments, 20.95 and 20.10 p. c. water (3 at. = 18.81 p.c.). The salt thus dried gave by analysis 30.20 p. c. carbon and 4.12 hydrogen, the formula  $C^{12}H^9CdO^{12}$  requiring 30.9 and 3.9.

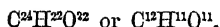
*Lead-salt.* —  $C^{12}H^9PbO^{12}, 4PbO + aq.?$  The aqueous acid mixed with ammoniacal sugar of lead yields a bulky white precipitate which becomes somewhat denser if left under the liquid.

				Barth & Hlasiwetz.	
12 C .....	72	....	9.82	9.16	
10 H .....	10	....	1.35	1.13	
5 PbO .....	557.5	....	70.30	71.37	
11 O .....	88	....	18.53	18.34	
$C^{12}H^9PbO^{12}, 4PbO + aq.$				727.5	100.00
				100.00	100.00

*Copper-salt.* — Carbonate of copper dissolves in the aqueous acid, forming an emerald-green liquid, which dries up to dark green transparent films.

*Silver-salt.* — Very strong solutions of the potash-salt and nitrate of silver yield an amorphous gelatinous precipitate which soon turns brown when exposed to light. It is soluble in water. Isobiglycol-thylenic acid dissolves in warm *alcohol*, and is precipitated therefrom in flocks by *ether*. ¶.

## Cane-sugar.



SCHRICKEL. *Diss. de Salib. saccharinis, &c.*, Giessæ. 1776.

CRUIKSHANK. *Scher. J.* 1, 637; 3, 289.

BOUILLON-LAGRANGE. *Ann. Chim.* 71, 91.

BERZELIUS. *Ann. Chim.* 95, 59.

KUHLMANN. *Ann. Chim. Phys.* 54, 323; *Ann. Pharm.* 9, 213; *J. pr. Chem.* 2, 235 (Preparation). — *Compt. rend.* 30, 341; *Dingl.* 116, 61 (the same).

PELIGOT. *Ann. Chim. Phys.* 67, 113; *J. pr. Chem.* 15, 65; *N. Br. Arch.* 15, 227; abstr. *Ann. Pharm.* 30, 69 (Decompositions by Heat. — Compounds with Bases). — *Ann. Chim. Phys.* 73, 103; *J. pr. Chem.* 17, 183; *Ann. Pharm.* 30, 91; *Compt. rend.* 8, 530 (Lead-compounds of Cane-sugar). — *N. J. Pharm.* 2, 103 (the

- same). — *Compt. rend.* 32, 333; *N. J. Pharm.* 19, 324; *Ann. Pharm.* 80, 342; *J. pr. Chem.* 52, 405; in detail: *N. Ann. Chim. Phys.* 54, 377 (Sugar-lime). — *Compt. rend.* 32, 421 (Analyses of Cane-sugars).
- VENTZKE. *J. pr. Chem.* 25, 64; 28, 101 (Polarisation).
- HOCHSTETTER. *J. pr. Chem.* 29, 1 (Decompositions).
- DUBRUNFAUT. *Ann. Pharm.* 17, 283 (Manufacture). — Inversion :  
 1. *Compt. rend.* 23, 38; in detail: *N. Ann. Chim. Phys.* 18, 99. —  
 2. *N. Ann. Chim. Phys.* 21, 169; *J. pr. Chem.* 42, 418; *Pharm. Centr.* 1849, 648. — 1 to 3 consecutively: *Compt. rend.* 32, 498. — Estimation: *Compt. rend.* 32, 249; *Pharm. Centr.* 1851, 278; *Dingl.* 121, 299. — *Compt. rend.* 32, 857; *J. pr. Chem.* 53, 508; *Dingl.* 121, 305.
- SOUBEIRAN. *N. J. Pharm.* 1, 1 and 89; *J. pr. Chem.* 27, 281 (Transformations of Sugar by Water and Heat). — *N. J. Pharm.* 1, 469; *Ann. Pharm.* 43, 223; *J. pr. Chem.* 26, 498 (Compounds with Lime, Baryta, and Lead). — *Compt. rend.* 28, 774; in detail: *N. J. Pharm.* 16, 252; *J. pr. Chem.* 49, 65 (Sugar in Honey). — *N. J. Pharm.* 19, 329 (Sugar-lime).
- MAUMENÉ. *Compt. rend.* 30, 314, and 447; *Pharm. Centr.* 1850, 349; *Compt. rend.* 39, 422; *J. pr. Chem.* 63, 75; *Chem. Centr.* 1854, 735; *Chem. Gaz.* 1854, 413 (Caramelin). — *Compt. rend.* 39, 914; *J. pr. Chem.* 64, 147; *Chem. Centr.* 1854, 920 (Action of Water). — *Compt. rend.* 42, 645; *J. pr. Chem.* 69, 256; in detail: *N. Ann. Chim. Phys.* 48, 23 (Preparation on the large scale). — *Compt. rend.* 45, 1021; *J. pr. Chem.* 74, 232 (Formation of Alcohols by Fermentation).
- Alcoholic or Vinous Fermentation: PASTEUR. 1. *Compt. rend.* 45, 1032; *J. pr. Chem.* 73, 451; *Chem. Gaz.* 1858, 61; *Kopp's Jahresber.* 1857, 508. — 2. *Compt. rend.* 46, 179; *J. pr. Chem.* 73, 457; *Ann. Pharm.* 105, 264. — 3. *Compt. rend.* 46, 857; *J. pr. Chem.* 73, 506; *Ann. Pharm.* 106, 338. — 4. *Compt. rend.* 47, 224; *J. pr. Chem.* 74, 512; *Chem. Centr.* 1858, 685. — 5. *Compt. rend.* 47, 1011; *J. pr. Chem.* 76, 369; *Chem. Centr.* 1859, 175; 2 to 5 also in *Kopp's Jahresber.* 1858, 484. — 6. *Compt. rend.* 48, 640; *Rép. Chim. pure*, 1, 310. — 7. Against Berthelot, *Compt. rend.* 48, 691, and 737. — 8. *Compt. rend.* 48, 735; *Rép. Chim. pure*, 1, 355; *Chem. Centr.* 1859, 671. — 9. *Compt. rend.* 48, 1149; *Rép. Chim. pure*, 1, 519; *Phil. Mag.* [4], 181, 239. — 6 to 9 also in *Kopp's Jahresber.* 1859, 549. The whole 1 to 9, *N. Ann. Chim. Phys.* 58, 323.
- Lactous Fermentation: PASTEUR. *Compt. rend.* 45, 913; *J. pr. Chem.* 73, 447; in detail: *N. Ann. Chim. Phys.* 52, 404; abstr. *Kopp's Jahresber.* 1857, 510. — *Compt. rend.* 47, 224; *Kopp's Jahresber.* 1858, 484. — *Compt. rend.* 48, 337; *J. pr. Chem.* 77, 27; *Kopp's Jahresber.* 1859, 553.
- M. BERTHELOT. Transformation by Salts: *Compt. rend.* 34, 800; *N. J. Pharm.* 22, 37; *Ann. Pharm.* 83, 104; in detail: *N. Ann. Chim. Phys.* 38, 57. — Solubility of Lime in Sugar-water: *N. Ann. Chim. Phys.* 46, 123. — Compounds with Acids: *Compt. rend.* 41, 452; *J. pr. Chem.* 67, 235. — *Compt. rend.* 45, 268; *N. J. Pharm.* 33, 95; *J. pr. Chem.* 73, 157; *Chem. Gaz.* 1857, 441; in detail: *N. Ann. Chim. Phys.* 54, 74. — Fermentation: *Compt. rend.* 43, 238; *N. J. Pharm.* 30, 269; *J. pr. Chem.* 69, 454. — *Compt. rend.* 44, 702; *J. pr. Chem.* 71, 321; in detail: *N. Ann. Chim. Phys.* 50, 322. — Occurrence: *Compt. rend.* 46, 1376; in detail: *N. Ann. Chim.*

*Phys.* 55, 286. — *Chimie organique fondée sur la synthèse*, Paris, 1860.

BÉCLAMP. Decomposition by Water and Salts: *Compt. rend.* 40, 436; *N. J. Pharm.* 27, 274. — *Compt. rend.* 46, 44; *J. pr. Chem.* 74, 495; in detail: *N. Ann. Chim. Phys.* 54, 28.

BUGNET. *N. Ann. Chim. Phys.* 61, 233.

*Common Sugar. Crystallisable Sugar. Sucre de canne. Rohrzucker.* — *Saccharose* (Berthelot). — Known in India and China, from very early times, and in Europe since the time of Alexander the Great. The culture of the sugar-cane was imported, in the fourteenth and fifteenth centuries, from Nubia, Arabia, and Egypt into Spain, Portugal, and the Canary Islands, afterwards to America: it was only after this last importation that it came into general use. The presence of cane-sugar in beet and other plants, indigenous in Europe, was first demonstrated in 1747 by Marggraf, and its preparation on the large scale from beet was introduced by Achard. An important auxiliary in the study of the different varieties of sugar was afforded by the phenomena of circular polarisation discovered by Biot.

*Sources.* In the vegetable kingdom universally diffused, existing apparently in many plants, from which, in consequence of the mode of examination formerly adopted, only fruit-sugar or grape-sugar had been obtained. In the stems of *Grasses*: Of the sugar-cane, *Saccharum officinarum*; of the Asiatic sugar-cane, *Sorghum saccharatum*; of maize, and probably also of other cereals. The juice of the sugar-cane contains more than 20 per cent. of cane-sugar, unmixed with any other kind of sugar. (Avequin; Plagne, *J. Pharm.* 26, 248; Peligot.) It contains no optically active substance except cane-sugar. (Clerget.) The stems of *Sorghum saccharatum*, when quite ripe, contain from 9 to 9½ p. c. cane-sugar, but no fruit-sugar (Gössmann, *Ann. Pharm.* 104, 335; *Henneberg's landw. Journal* 6, 294); Bergemann found only fruit-sugar; Lüdersdorff and Fehling found cane-sugar and fruit-sugar. (*Henneberg's landw. Jahresh.* 1854, 245.) The unripe stems contain only fruit-sugar and starch, which latter disappears in the process of ripening, in proportion as cane-sugar makes its appearance. (Jackson, *Compt. rend.* 46, 55; Leplay, *Compt. rend.* 46, 444.) — The juice of maize-stems cut at the time of ripening, is especially rich in cane-sugar, if the female flowers have been removed during the flowering season; it appears to contain a little glucose as well as cane-sugar. (Soubeiran & Biot, *Compt. rend.* 15, 523; Pelouze, *Compt. rend.* 15, 580.) Maize-stems cut shortly after the flowering of the plant, contain a quantity of sugar amounting to between 7.4 and 7.9 p. c. of the juice, and about half consisting of cane sugar. (Lüdersdorff.)

In the *fleshy roots* of *Angelica archangelica* (A. Buchner), *Beta vulgaris*, *Charophyllum bulbosum* (Payen), *Cichorium Intybus*, *Daucus Carota*, *Helianthus tuberosus*, *Leontodon taraxacum*, *Pastinaca sativa*, *Sium Sisarum*, and others. — Field beet or mangold-wurzel contains, on the average, between 7 and 11 p. c., in particular cases as much as 14 p. c. of cane-sugar, the proportion varying with the kind of manure employed, the locality, and the variety and size of the beet, the largest quantity being yielded by the white Silesian sugar-beet. Small kinds are generally richer in sugar than the larger. In one and the same beet,

the leaf-head contains the smallest, the middle of the fleshy stem the largest amount of sugar, Beet contains no other sugar than cane-sugar (Payen, *Compt. rend.* 15, 618), but it contains another optically active substance which is not altered by acids. (Clerget, *N. Ann. Chim. Phys.* 26, 175.) (On the variations in the amount of sugar under different influences, see *Henneb. landw. Jahresber.* 2 Abth. 1853, 27; 1854, 23; 1859 and 1856, 31.) — In the tubers of *Lathyrus tuberosus* (Braconnot); in the sweet potato of St. Domingo (of *Convolvulus batatas*). Avequin (*J. Pharm.* 21, 548).

In the stem of the sugar-maple, *Acer saccharinum*, of the sycamore, *Acer Pseudoplatanus*, and other species of *Acer* (Cadell, *Thoms. Ann.* 10, 234); of some species of *Betula* (Schleiden); in the vernal juice of *Juglans alba* (Bigelow, *Scher. Ann.* 8, 118); of *Tilia europæa* (Riegel, *Jahrb. pr. Pharm.* 14, 155). In several palms, especially the *Saguerus Rumphii* of Java (Berthelot, *N. Ann. Chim. Phys.* 55, 286; comp. Pereira, *N. J. Pharm.* 9, 345.)

*In Fruits.* The sugar which forms in fruits at the season of maturity is always cane-sugar; under the influence of a peculiar kind of ferment, (*vid. inf.*, p. 254) however, it may be converted wholly or partially into inverse sugar; so that the ripe fruit sometimes contains only inverse sugar, sometimes both kinds together. Figs, grapes, cherries, Spanish cherries, strawberries, of the variety called *Princesse royale*, and gooseberries, contain no cane-sugar, but only inverse sugar; other fruits contain both kinds in various proportions. (Buignet.) The lævo-rotatory (inverse) sugar of grapes deposits on standing dextro-rotatory grape-sugar, and retains its lævo-rotatory power, even in the dried grape, with liquid or granular contents. If syrup of grape-juice turns the plane of polarisation to the right, it is in consequence of alterations which have especially affected the lævo-rotatory fruit-sugar. Thus the *Acarus farinæ* and ants devour the lævo-rotatory fruit-sugar and leave dextro-rotatory grape-sugar behind. (Dubrunfaut, *Compt. rend.* 29, 54.) Oranges, ripe or unripe, contain both kinds of sugar, the relative proportion of the two changing during the process of maturation. The quantity of inverse sugar remains nearly the same, but that of cane-sugar increases in proportion to the total weight of the solid matters as well as of the inverse sugar. (Berthelot & Buignet, *Compt. rend.* 51, 1094.) Apples and pears contain cane-sugar, and either a peculiar lævo-rotatory sugar, or more probably inverse sugar, which, before the time of the observation, undergoes an irregular decomposition, first attacking the dextro-rotatory grape-sugar (as in Dubrunfaut's fermentation experiment), and thereby giving the preponderance of rotatory power to the lævo-rotatory fruit-sugar, formed from the inverse sugar. (Buignet.) — Unripe bananas contain a peculiar tannin, starch, and cane-sugar, the quantity of the last increasing as the fruit ripens in proportion as the other two disappear. In bananas artificially ripened after their removal from the tree, the tannin and starch have likewise disappeared; on the other hand, they contain 15 p.c. sugar, one-third consisting of cane-sugar, and the remaining two-thirds of inverse sugar, which latter appears to be formed from starch during the process of vegetation, and is present instead of cane-sugar in the artificially ripened fruit. The formation of cane-sugar in fruits is not prevented by the presence of acids. (Buignet.) The sugar of fruits was formerly regarded as distinct from cane-sugar; but the presence of cane-sugar has been demonstrated in melons by

Payen; in bananas by Avequin (*J. Pharm.* 24, 556), and in dates by Bonastre (*J. Pharm.* 18, 725). On the amount of sugar in various kinds of fruit, see Fresenius, *Ann. Pharm.* 101, 219; Buignet, *N. Ann. Chim. Phys.* 61, 243.

Walnuts, hazel-nuts, bitter almonds, and sweet almonds contain only cane-sugar (Pelouze, *Compt. rend.* 40, 608); also the carob bean or St. John's bread, the fruit of *Ceratonia Siliqua* (Berthelot), and coffee-beans (Stenhouse, Graham & Campbell, *Chem. Soc. Qu. J.* 9, 33; *Chem. Centr.* 1857, 54).

The nectar of the flowers of *Rhododendron ponticum* contains cane-sugar (G. Jäger, *Tiedemann's Zeitschr. f. Physiol.* 2, 173), which is even found in crystals in the flowers of this plant. (Sthamer, *N. Br. Arch.* 59, 151.) The nectar of various kinds of cactus contains scarcely anything but cane-sugar, that of other flowers likewise contains fruit-sugar. (Braconnot, *J. Chim. méd.* 19, 3; *J. pr. Chem.* 30, 363; comp. Ludwig, *N. Br. Arch.* 107, 10.)—The honey of *Polybia apicipennis*, an American wasp, yields crystals of cane-sugar. (Karsten, *Pogg.* 100, 550; *J. pr. Chem.* 71, 315.) Common bees' honey contains lævo-rotatory fruit-sugar (in excess, according to Dubrunfaut), dextro-rotatory grape-sugar, and cane-sugar; the latter is found more frequently in the liquid honey as it exists in the cells, and disappears almost entirely when the honey is kept. (Soubeiran, *N. J. Pharm.* 16, 253; *J. pr. Chem.* 49, 65; abstr. *Compt. rend.* 28, 775; *Lieb. Kopp. Jahresber.* 1849, 465.) The cane-sugar of fresh honey is inverted during keeping by the action of the adhering ferment, and may then deposit from 20 to 30 per cent. of dextro-rotatory grape-sugar, while lævo-rotatory fruit-sugar remains behind. (Dubrunfaut, *Compt. rend.* 29, 51.)

It is doubtful whether *panoche-sugar* should be regarded as a kind of cane-sugar. It is found on the surface of the leaves of a Californian sugar-cane, and appears to be juice exuded in consequence of the punctures of insects and dried (Johnson, *Sill. Ann. J.* [2], 22, 6; *Chem. Centr.* 1856, 764; *N. Br. Arch.* 93, 54; *J. pr. Chem.* 70, 245).

¶. Manna from Sinai (the produce of *Tamarix mannifera*) contains 55 p. c. cane-sugar, 25 inverse sugar and 20 dextrin &c.; manna from Kurdistan contains 61 p. c. cane-sugar, 16.5 inverse sugar, and 22.5 dextrin &c. (Berthelot, *Compt. rend.* 53, 583; *Rép. Chim. pure*, 4, 29.) ¶.

The bark of *Pinus sylvestris* contains a sugar which is obtained in the preparation of pinicorretin (p. 33), but is somewhat difficult to crystallise on account of impurities. This, after drying at 100°, contains 39.68 p. c. C., 6.92 H., and 53.40 O. corresponding to the formula  $C^{12}H^{12}O^{12}$ .—In the preparation of pinipicrin from pine-needles (vid. inf.) a sugar is obtained, which, when purified by dissolving it in aqueous alcohol, evaporating the filtrate, washing the crystals with ether-alcohol, and drying at 100°, contains 42.3 p. c. C., 6.73 H., and 50.98 O., corresponding to the formula of cane-sugar (Kawaller, *Wien. Akad. Ber.* 11, 364 and 353). The former sugar should perhaps be classed with inverse sugar, the latter with cane-sugar. (Kr.)

In healthy *cereals*, and even in *barley-malt*, sugar does not exist ready formed, but is rather produced, in the crushed grain, by the action of diastase and water (Mitscherlich, *N. J. Pharm.* 4, 213; Peligot, *N. Ann. Chim. Phys.* 29, 5; Stein, *Polyt. Centr.* 1860, 181). The sugar thus produced is perhaps maltose. (Kr.)

*Preparation.* From the juice of the Sugar-cane, of *Sorghum saccharatum*, and of *Mangold-wurzel*. The juice of the sugar-cane is obtained by pressure, that of mangold-wurzel by reducing the roots to a fine pulp, and either pressing this pulp after adding a quantity of water equal to 20 per cent. of the weight of the root, or lixiviating it with cold water, or finally by subjecting it in perforated cylinders to the rotatory action of the centrifugal machine. — The juice of mangold-wurzel is heated to  $68^{\circ}$  by hot steam, every 1000 quarts are mixed with a quantity of milk of lime prepared from 12 lbs. of lime, and the mixture is further heated to the boiling point, whereby phosphate of lime, albumin, albuminate of lime and other matters are separated in the form of a dense white crust. The heating is interrupted as soon as the boiling juice begins to break through the crust, the clear liquid below is run off, and the muddy residue is submitted to pressure. The calcareous *thin syrup* (*Dünnsaft*) thus obtained is treated with carbonic acid (from 0.6 to 0.8 p. c. lime however remains dissolved as sugar-lime); separated by subsidence and decantation from precipitated carbonate of lime; filtered through bone-black, which removes a small quantity of sugar-lime, and evaporated to  $20-22^{\circ}$  Bm., either in open pans or in Robert's vacuum apparatus. The *thick syrup* (*Dicksaft*), again filtered through bone-black, and evaporated in vacuo at about  $22''$  barometric pressure till it becomes thick enough to draw out into threads, yields, after cooling and standing, crystals of cane-sugar, and the mother-liquor, when further evaporated, yields a second and third crop, till nothing remains but uncrystallisable *molasses*. The last very dark-coloured crop of crystals is moistened with water, and freed from adhering molasses by means of the centrifugal machine. The mixture of all the successive crops of crystals thus obtained constitutes the *raw sugar* of commerce.

*Purification. Refining of cane-sugar.* An aqueous solution of cane-sugar of  $12^{\circ}$  Bm. is mixed with a small quantity of milk of lime, and heated to the boiling point, and the juice is decanted from the impurities which separate in the form of a crust, then filtered through bone-charcoal, and evaporated in vacuo. The strongly concentrated juice is made to crystallise by moderating the heat and running in small quantities of unthickened juice, whereupon a magma of sugar-crystals immediately forms. To give them the requisite hardness, heat is again applied, the crystalline magma is left to drain in the sugar-loaf moulds, and the formation of small uniform crystals is promoted by stirring and breaking up the crust which forms on the surface. When the crystallisation is complete, the apex of the mould, which has previously been closed, is opened to allow the syrup to drain off, and that which remains adhering to the crystals is displaced by pouring in pure sugar-syrup. By due desiccation, the *loaf-sugar* or *refined sugar* of commerce is obtained. When purified sugar-syrup is left to evaporate slowly and quietly in shallow vessels, in which threads are suspended, the sugar is obtained in larger crystals, called *sugar candy*.

Formerly, ox blood, milk, or white of egg was used for clarifying syrups. On the use of larger quantities of lime in the preparation of sugar, see Kuhlmann (*Ann. Pharm.* 27, 17; *Dingl.* 116, 61); Rousseau (*Inst.* 1850, 330; *Dingl.* 115, 457; 116, 297; 118, 221; 125, 378); Maumené (*N. J. Pharm.* 30, 354; *N. Ann. Chim. Phys.* 48, 23; *Dingl.* 143, 285). — On the use of bisulphite of lime in the refining of sugar, previously recommended by Proust, Dubrunfaut & Stolle, see *Lieb. Kopp. Jahresber* 1849, 700; Dumas & Meisens (*Dingl.* 114, 375; 115, 212); Meisens (*N. Ann. Chim.*

*Phys.* 27, 273; *Ann. Pharm.* 72, 101; Report on its applicability, *Dingl.* 119, 448.) On the use of sulphurous acid, see Calvert (*Dingl.* 149, 136); of acetate of lead and sulphurous acid, Scoffern (*Dingl.* 110, 261; 118, 217; *Chem. Gaz.* 1850, 368; *Pharm. J. Trans.* 10, 108, and 184; also *Lieb. Kopp. Jahresber.* 1850, 680).—On the freeing of syrup from lime by soap, see Basset (*Dingl.* 147, 129), also Stahlschmidt (*Dingl.* 149, 211); by hydrate of alumina, see Howard (*Dingl.* 19, 384), Mène (*Dingl.* 146, 309), Cessner & Kletzinsky (*Dingl.* 140, 376); by phosphate of alumina, Daubeny (*J. pr. Chem.* 75, 255); by phosphate of ammonia, Kuhlmann (*Dingl.* 116, 61); by acid phosphate of lime, carbonate of ammonia, stearic acid or oleic acid, Stammer (*Dingl.* 154, 210); by stearic acid and silicic acid, Wagner (*Dingl.* 153, 377). On the use of chloride of calcium, see Michaelis (*J. pr. Chem.* 56, 435).

*From Molasses.* According to Lepray & Dubrunfaut. A solution of caustic baryta of 30° Bm. is poured into the molasses, whereupon the whole solidifies to a crystalline pulp. This is washed, treated with carbonic acid, and freed from carbonate of baryta by filtering and decantation. A syrup of 18° — 22° Bm. is thus obtained, which is freed from the last traces of baryta by means of gypsum or sulphate of alumina, then clarified and boiled down as above. (Nicklès, *Dingl.* 131, 47.)

*On the small scale.* The best process, according to Marggraf, is to dry and pulverise the sacchariferous portion of the plant, boil it with 2 pts. of strong alcohol, filter, and leave it to cool. The filtrate set aside for some time yields crystals of sugar.

*From Fruits likewise containing Inverse Sugar.* The expressed fruit-juice is filtered (after addition of an equal quantity of alcohol if necessary in order to prevent alterations), then saturated with slaked lime and again filtered. The filtrate heated to the boiling point and again filtered at that temperature, leaves on the filter insoluble sugar-lime, which after thorough washing with water, is decomposed by carbonic acid. The sugar-solution is evaporated to a syrup, decolorised with animal charcoal, mixed with alcohol till it becomes turbid, and left to crystallise over quicklime. The insoluble sugar-lime produced at the boiling heat cannot include more than  $\frac{2}{3}$  of the total quantity of sugar present; hence the treatment with lime must be repeated.—If the decomposition of the sugar-lime with carbonic acid yields very turbid liquids, they must be precipitated with basic acetate of lead and the filtrate treated with sulphuretted hydrogen. (Buignet.)

*Estimation of Cane-sugar. Saccharimetry.* If the solution contains nothing but cane-sugar, the specific gravity is observed, and the percentage of sugar determined therefrom (*vid. inf.*). If other substances which affect the density are likewise present, the quantity of cane-sugar may be determined:—1. From the weight of carbonic acid, formed in the vinous fermentation of the sugar, or from the quantity of alcohol thereby produced. According to older statements, 100 pts. cane-sugar yield, after deduction of 5.26 pts. water, 51.44 pts. carbonic acid, and 53.80 absolute alcohol) according to Pasteur's direct determination, 49.12 pts. carbonic acid and 51.01 absolute alcohol, the remaining portion of the sugar being consumed in the formation of glycerin and succinic acid. See below; also Buignet's description of the process (*N. Ann. Chim. Phys.* 61, 239).—2. From the weight of cuprous oxide which the sugar can reduce from potassio-cupric tartrate, or from the volume of a standard solution of that salt decomposed by the sugar. For this re-action, the cane-sugar must be previously heated with acids to convert it into inverse sugar, which reduces the same quantity of cupric oxide as grape-sugar (see *Grape-sugar*).—3. *From the Rotatory Power of the solution.* If the solution contains only cane-sugar, or at least, no



other optically active substance, the amount of sugar may be calculated from the rotatory power in the manner presently to be described (p. 246). Turbid or gummy solutions are mixed with  $\frac{1}{10}$  their volume of isinglass-solution, then, after agitation, with  $1\frac{1}{2}$  vol. alcohol, whereupon the mixture, without being heated, coagulates, and yields a filtrate adapted for observation. Coloured solutions are decolorised by animal charcoal; but as this substance (according to some statements) takes up sugar, the first fourth of the liquid that runs through is rejected, and only the remainder used for the observation. — If in addition to cane-sugar, the solution contains grape-sugar (inverse sugar, or any other optically active substance, whose rotatory power is not altered by heating with acids), the amount of cane-sugar may be determined by observing the rotatory power of the solution both before and after inversion (p. 244), the temperature being likewise observed in the latter case. The first observation having been made, 100 c. c. of the solution are mixed with 10 c. c. fuming hydrochloric acid, the mixture heated to  $68^\circ$ , and kept at that temperature for a quarter of an hour. Since the rotatory power of the solution cooled to the original temperature (supposing the observation to have been made in a tube longer by one-tenth than the former), remains unaltered in so far as it was due to the grape-sugar, whereas the cane-sugar has been replaced by inverse sugar, the amount of cane-sugar may be calculated from the rotatory power peculiar to this inverse sugar, as follows:—The rotatory power ( $a$ ) observed before inversion was made up of the molecular rotatory power ( $c$ ) of the cane-sugar ( $C$ ), and that of the grape-sugar ( $g$   $G$ ); therefore

$$a = cC + gG.$$

The rotatory power ( $a'$ ) observed after inversion is, in like manner, made up of the unaltered rotatory power of the grape-sugar ( $g$   $G$ ), and that of the inverse sugar ( $i$   $C$ ); therefore

$$a' = iC + gG.$$

Consequently the difference,  $a - a'$ , of the rotations observed before and after inversion is equal to  $cC - iC$ .

$$a - a' = C(c - i).$$

or, finally,—

$$C = \frac{a - a'}{c - i}$$

Suppose for example a sugar-solution before inversion turns the plane of polarisation  $25.96^\circ$  to the right, and after inversion,  $5.80^\circ$  to the right at a temperature of  $14^\circ$ ; then  $a = 25.96$  and  $a' = 5.80$ . Now the molecular rotatory power of cane-sugar ( $c$ ) is  $73.8^\circ$ , that of grape-sugar  $56^\circ$ , that of inverse sugar (or more exactly, the rotatory power of that quantity of inverse sugar which would be produced from the unit of weight of cane-sugar adopted in determining the molecular rotatory power of cane-sugar) is  $-27^\circ$  at the temperature of  $14^\circ$ : consequently

$$C = \frac{25.96 - 5.80}{73.8 + 27} \quad \text{or} \quad C = \frac{20.16}{100.8} = 0.20,$$

which quantity therefore gives the number of parts by weight of cane-sugar contained in a unit of weight of the solution employed, or when multiplied by 100, the percentage of cane-sugar in the solution.

Suppose another sugar-solution, before inversion to turn the plane of polarisation  $9.36^\circ$  to the right, and after inversion  $10.80^\circ$  to the left ( $= -10.80^\circ$  to the right). In this case,  $\alpha = 9.36$ ;  $\alpha' = -10.80$ ;  $\alpha - \alpha' = 9.36 + 10.80 = 20.16$ , which number divided by 100.8 again gives 0.2, or 20 p. c. of cane-sugar in the solution. If, in both cases, the nature of the second optically active substance present in addition to the cane-sugar is known, its quantity may be determined from the observations just described; if, on the other hand, its quantity is previously known, its nature may be determined; thus it might be inferred that grape-sugar was present in the first case, besides the cane-sugar, in the original solution, and inverse sugar in the second. This mode of proceeding, however, is admissible, only when the deflection after inversion has been observed at a temperature for which the molecular rotatory power of the inverse sugar (which varies with the temperature, has been previously determined. According to Biot (*Compt. rend.* 15, 523, 619, and 694; 17, 755) and Clerget. See Clerget's method (*N. Ann. Chim. Phys.* 26, 175; *Ann. Pharm.* 72, 145; abstr. *Compt. rend.* 23, 259; *Lieb. Kopp. Jahresber.* 1849, 126). This method presupposes the use of Soleil's saccharimeter, and Clerget denotes by 100 the deflection produced by 1 mm. quartz, or 200 mm. of a normal sugar-solution containing 16.471 grm. cane-sugar in 100 cubic centimetres.

*Properties.* Large, transparent, colourless crystals, belonging to the monoclinic system. Fig. 83 without  $t$ . Combination of a rhombic prism  $u$  with the acute lateral edges of the oblique basic end-face  $i$ , truncated by  $m$ . More complex crystals likewise exhibit a back oblique end-face  $f$  (Fig. 84) as well as the front oblique end-face  $f$  (not shown in the figure) between  $i$  and  $m$ ; also the prism  $\alpha$  parallel to the clinodiagonal, for the most part developed on the left side only. The crystal-electricity ( $i$ , 319) takes the direction of these faces (according to Hanke), inasmuch as when the temperature is lowered, the antilogous (negative) pole appears on that side of the crystal on which the two  $\alpha$  faces are developed.—Rammelsberg obtained the prism  $\alpha$  perfectly developed from a solution containing chloride of sodium. He further observed the octahedral faces  $o$  (which truncate the edges  $i:u$  and lie in the same zone with  $m$ ) corresponding to the similarly situated  $o'$ -faces behind. These two faces have hitherto been found only on the left side. The crystals are generally tabular, from the extension of  $m$  in the direction of right and left:— $u:u = 101^\circ 32'$  (Wolff),  $101^\circ 30'$  (Rammelsberg);  $m:i = 103^\circ 30'$  (W.),  $103^\circ 17'$  (R.);  $m:f' = 134^\circ 23'$  (R.);  $i:f = 140^\circ 40'$  (R.);  $m:f = 115^\circ 33'$  (R.);  $i:f = 141^\circ 0'$  (W.),  $141^\circ 43'$  (R.). Cleavage distinct parallel to  $m$ . Twin crystals have the faces  $m$  common to both, the oblique summits  $i$  lie reversed, and the left sides of the crystals are turned towards each other. The plane of the optic axes is perpendicular to  $m$  and  $i$  (Miller, *Pogg.* 56, 630); one optic axis makes, with the perpendicular to  $m$ , an angle of about  $1^\circ 26'$  towards the lower side; the other lies about  $50^\circ$  above it. (Wolf, *J. pr. Chem.* 28, 129; Rammelsberg, *Handbuch*, Berlin, 1855, 397; comp. also von Kobell, *Repert.* 34, 279; Hankel, *Pogg.* 49, 495; Kopp, *Einleitung*, Braunschweig, 1849, 312; Berthelot, *N. Ann. Chim. Phys.* 55, 287.)

Molecular rotatory power\*  $[\alpha]_j = 73.84$  to the right (Dubrunfaut,

\* We must here add to what has been already said (vii. 64) about circular polarisation, the explanation of the expressions used in the text, — *molecular rotatory power*, *specific rotatory power*, or of the symbol  $[\alpha]$  used to stand for these expressions. By

*Compt. rend.* 42, 901); 71.26, or  $[\alpha]_r = 54.636$  (Biot, *Compt. rend.* 15, 625 and 706). According to Dubrunfaut, Biot's cane-sugar was not perfectly pure. Comp. also Wilhelmy (*Pogg.* 81, 527, *Lieb. Kopp. Jahresber.* 1850, 176). The rotatory power varies but little with changes of temperature. (Ventzke.)

Sp. gr. 1.6065 (Fahrenheit), 1.63 (Dubrunfaut.), 1.593 at 3.9° (Joule & Playfair, *Chem. Soc. Qu. J.* 1, 121); sp. gr. of the crystals. 1.58, of the powder, 1.61 (Kopp); of sugar-candy, 1.58933 at 13°, of melted barley-sugar, 1.5092 (Biot, *Ann. Pharm.* 52, 195). Harder than any other kind of sugar except milk-sugar; emits light when struck in the dark.

molecular rotatory power is understood the number of degrees through which a stratum of the pure substance, 100 millimetres thick, would rotate the plane of polarisation, supposing its sp. gr. were = 1. This  $[\alpha]$  being known, the rotation  $a$  of the plane of polarisation, caused by a stratum, 100 mm. thick, of a solution containing  $\epsilon$  grammes of substance in 1 gramme solution is expressed by  $a = \epsilon[\alpha]$ , supposing that the sp. gr. of the solution is 1. If, however, the sp. gr. =  $\delta$ , we have  $a = \epsilon[\alpha]\delta$ . If the thickness of the stratum is  $\lambda$  times 100 mm.,  $a$  finally becomes =  $\epsilon[\alpha]\delta\lambda$ .—If the rotation  $a$  has been found by experiment, the quantity of substance  $\epsilon$  in 1 gramme solution, and hence the percentage contained in the solution, is given by the equation  $\epsilon = \frac{a}{[\alpha]\delta\lambda}$ .—If, on the other hand, it is desired to determine the molecular rotatory power  $[\alpha]$ , we have the equation  $[\alpha] = \frac{a}{\epsilon\delta\lambda}$ .

*Examples.* 1. The specific gravity of a solution of grape-sugar ( $[\alpha] = 57.6$ ) is found to be 1.048, and its rotatory power, in a tube 2 decimetres long, 13.7 degrees. Hence 1 gramme of the solution contains  $\epsilon = \frac{13.7}{57.6 \times 2 \times 1.048} = 0.11347$  grms. grape-sugar, or the solution contains 11.347 p. c.

2. By dissolving 11.347 grms. grape-sugar in 88.653 grms. water, a solution is obtained whose sp. gr. is 1.048, and whose rotatory power, in a tube 2 decimetres long, is 13.7 degrees. Hence the molecular rotatory power of grape-sugar is given by the equation:—

$$[\alpha] = \frac{13.7}{0.11347 \times 2 \times 1.048} = 57.6.$$

If (as is usually the case) the solution is prepared by weighing out a certain quantity of substance and making up the solution to a known measure, either the specific gravity must be determined, and hence the percentage amount contained in the solution calculated; or else (according to Berthelot) the molecular rotatory power is calculated from the observed rotation ( $a$ ), the weight in grammes ( $p$ ) of the dissolved substance, the volume of the solution in cubic centimetres ( $V$ ) in which  $p$  is contained, and the length ( $l$ ) of the tube expressed in decimetres, by aid of the formula (deduced from that given above),—

$$[\alpha] = a \frac{V}{lp}.$$

*Example.* 11.892 grms. grape-sugar is dissolved in water, the solution made up to 100 cubic centimetres, and the rotation is found to be 13.7 degrees in a tube of 2 decimetres. Hence the molecular rotatory power is—

$$[\alpha] = 13.7 \frac{100}{2 \times 11.892} = 13.7 \times 4.205 = 57.6.$$

The statements in the text relative to the value of  $[\alpha]$  apply either to the red ray, and are then denoted by  $[\alpha]_r$ , or to the yellow ray (equivalent to the transition-tint between blue and violet), and are then denoted by  $[\alpha]$  or  $[\alpha]_j$ . Almost all the modern determinations refer to the transition-tint; those which refer to the red ray become comparable with the others, according to Biot, after multiplication by  $\frac{23}{25}$ . (Kr.)

<i>In vacuo, or at 100°.</i>				Berzelius.	Liebig.	Erdmann & Marchand.			
24 C .....	144	...	42·11	...	41·48	...	42·30	.....	42·15
22 H .....	22	...	6·43	...	7·05	...	6·45	.....	6·47
22 O .....	176	...	51·46	...	51·47	...	51·25	.....	51·38
<hr/>									
C <sup>24</sup> H <sup>22</sup> O <sup>22</sup> .....	342	...	100·00	...	100·00	...	100·00	.....	100·00

Many other chemists have also analysed cane-sugar; for example Prout, Gay-Lussac & Thénard, Döbereiner, W. Crum, Berthollet, Herrmann, Brunner (*Pogg.* 34, 333), O. Henry & Plisson (*J. Pharm.* 16, 597), Erdmann & Marchand (*J. pr. Chem.* 23, 174), Peligot (*Ann. Chim. Phys.* 67, 113).

Sugar-candy and refined sugar prepared from mangold-wurzel, cane-, and maple-sugar have been examined with like results.

Liebig (*Pogg.* 31, 341; *Ann. Pharm.* 9, 21) first gave the correct formula, deducing it from the products of decomposition. This formula was adopted by Berzelius (*Jahresber.* 15, 291). Earlier formulæ: C<sup>12</sup>H<sup>11·5</sup>O<sup>11</sup> (Berzelius), C<sup>6</sup>H<sup>6</sup>O<sup>6</sup> (Döbereiner), C<sup>6</sup>H<sup>5</sup>O<sup>5</sup> (Dumas & Boullay), C<sup>6</sup>H<sup>5</sup>O<sup>5</sup> (Prout.)

*Decompositions.* 1. Cane-sugar melts at 160° or 161° (at 180°: Peligot), without losing weight, to a clear, pale yellow liquid, from which only part of the sugar can be regained in the crystallised form. (Berzelius, *Pogg.* 47, 321). If the melted mass is kept at the same temperature for a long time, it is decomposed, without loss of weight, into levulosan and dextro-glucose; C<sup>24</sup>H<sup>22</sup>O<sup>22</sup> = C<sup>12</sup>H<sup>10</sup>O<sup>10</sup> + C<sup>12</sup>H<sup>12</sup>O<sup>12</sup>. (Gélis.)

Melted sugar has the appearance of fruit-sugar, but reduces only half as much potassio-tartrate of copper as an equal weight of glucose. Only one-half of it is fermentable, the glucose being destroyed by fermentation and the levulosan remaining in solution. It deflects the plane of polarisation  $[\alpha]_D = 35^\circ$  to 38° to the left, about as much as a mixture of equal atoms of levulosan and glucose would deflect it. (Gélis, *Compt. rend.* 48, 1062.)

Sugar, melted in a chloride-of-zinc bath at 160°, has a smaller molecular rotatory power than cane-sugar, does not crystallise again, deliquesces in the air, is easily soluble in absolute alcohol, and ferments with yeast. (Mitscherlich, *Pogg.* 55, 222; *Berz. Jahresber.* 22, 482.) Melted sugar has not the same specific heat as cane-sugar (Herrmann, *J. pr. Chem.* 12, 295), nor amorphous sugar the same melting point as crystallised sugar. (Wöhler, *Ann. Pharm.* 51, 755.)—When cane-sugar is melted with a little water, as for the preparation of barley-sugar or of bonbons, at a temperature which does not exceed 165°, it solidifies on cooling to a vitreous mass, consisting mainly of cane-sugar containing enclosed water. In the course of time, this water dissolves particles of the cane-sugar, which afterwards crystallise out (because an amorphous body is more easily soluble in water than a crystallised body), until, by continued alternate solution and crystallisation, the whole mass has become crystalline. (Mitscherlich.) If melted sugar in the vitreous state is allowed to cool to 38°, and then quickly and often drawn out, doubled together and drawn out again until it forms a mass of threads, its temperature rises in two minutes from 40° to 80°, and it becomes a crystalline mass. Barley-sugar and bonbons are transformed into a similar mass by long keeping. (Graham.)—Cane-sugar melted with a very small quantity of water acidulated with acetic acid, so that it solidifies to a vitreous mass of sp. gr. 1·509, rotates the plane of polarisation more feebly than unaltered cane-sugar, and somewhat more feebly in the solid state than when again dissolved. (Biot, *Ann. Pharm.* 52, 195.)

Cane-sugar, heated above  $180^{\circ}$ , becomes brown and loses weight, and, if then exposed to the air, absorbs more water than it had lost, deliquesces, and behaves with alkalis like glucose. (Peligot.) Browning first takes place when the sugar is continuously heated to  $160^{\circ}$ ; no loss of weight occurs, because the water which is set free converts the still remaining levulose into lævo-glucose. (Gélin.)

Cane-sugar, heated for a long time to between  $210^{\circ}$  and  $220^{\circ}$ , froths up, becomes continually darker and darker brown, evolves a large quantity of water containing traces of acetic acid and volatile oil (furfural: *Völckel*), and, when the frothing has ceased, is converted into caramel, with which unaltered sugar and a bitter substance (assamar) are sometimes mixed. At a higher temperature, or when the heat is too long continued, further loss of water occurs and a substance insoluble in water is produced. (Peligot.) At  $250^{\circ}$  the residue of the sugar is still for the most part soluble in water, and only a small quantity of the insoluble substance (*Völckel's* caramelene) is formed; this body is produced more abundantly between  $250^{\circ}$  and  $300^{\circ}$ , products of further decomposition being formed at the same time. (*Völckel*.) As low as  $190^{\circ}$ , three products are successively produced from cane-sugar; the first of them, *caramelene*, constitutes the chief part of the residue when the loss of weight amounts to 10 p. c.; when the loss is 14 or 15 p. c., *caramelene* is obtained; when it amounts to 20 p. c., scarcely anything but *carameline*. (Gélin.) Reichenbach's assamar is also produced by the roasting of cane-sugar (by heating to  $225^{\circ}$ : *Pohl*). See also Mulder (*J. pr. Chem.* 16, 245).

On treating with alcohol the residue obtained by heating cane-sugar or glucose in an oil-bath to  $210^{\circ}$  or  $220^{\circ}$ , unaltered sugar and bitter tasting substances, are dissolved, and Peligot's *caramel* remains behind as a tasteless, black, shining mass, containing when dried at  $180^{\circ}$ , on an average, 46.65 p. c. carb., 6.18 hydr., and 47.17 oxyg., corresponding to the formula  $C^{24}H^{18}O^{18}$ , which requires 47.06 p. c. carb., 5.88 hydr., and 47.06 oxyg. It is soluble in water, precipitable by baryta-water and ammoniacal sugar of lead, not fermentable, and insoluble in alcohol. (Peligot.) See also Pohl. (*Wien. Akad. Ber.* 41, 623; *J. pr. Chem.* 82, 148.)

If the caramel is extracted by water from the residue obtained by heating cane-sugar to  $250^{\circ}$ , *caramelene* remains as a black substance insoluble in alcohol, partially soluble in potash-ley, containing 55.09 p. c. carb., 5.14 hydr., and 39.77 oxyg., answering to the formula  $C^{24}H^{18}O^{18}$ , which requires 55.17 p. c. carb., 4.98 hydr., 39.85 oxyg. (*Völckel, Ann. Pharm.* 85, 94.) According to Gélin, both these substances are mixtures: *vid. infr.*

Reichenbach's *Assamar* (Comp. *Völckel's* Assamar, p. 50). The bitter substance produced by roasting sugar. — It is formed by the roasting of gum, starch, gluten, gelatin, albumin, and flesh, and in the roasting, baking, or frying of eatables containing these substances. — Reichenbach heats either of these substances, — unsalted wheat-bread answers best, — on a hot hearth-plate, until it becomes brown; breaks it up while still warm; allows the powder to cool out of contact with air; and exhausts it with absolute alcohol. He separates the alcohol by distillation; heats the residue moistened with water to  $100^{\circ}$ ; allows it to cool very slowly; removes the fat which has separated out; neutralises with milk of lime; heats to boiling, and adds, by small portions at a time, 20 or 30 measures absolute alcohol, or so much that the precipitate

which is at first produced does not re-dissolve, even on boiling. After removing the alcohol from the cooled clear solution by distillation, the residue is repeatedly dissolved in hot alcohol as often as anything is deposited from the solution on cooling; ether is added to the clear solution in small quantities, as long as the precipitate produced has a sweet taste; and the assamar, which remains dissolved through all these operations, is obtained by evaporating the ether and alcohol, and finally drying in small quantities. — Solid, transparent, amber-yellow, amorphous gum, brittle and having a conchoidal fracture. Neutral. — It is decomposed when *heated* alone or with water, loses its bitterness, and is transformed into the substance which is separated by alcohol in the preparation of assamar. — Assamar is decomposed by *chlorine*, when heated, losing its colour; by hot *nitric acid*, without formation of mucic or of oxalic acid; by *oil of vitriol* with blackening, not by dilute sulphuric acid. Not altered by cold *potash-ley*; when boiled therewith it loses its bitterness, which acids do not restore. It reduces *nitrate of silver*, throws down a blue-black precipitate from *chloride of gold*, and cuprous oxide from *acetate*, not from *sulphate of copper*. Not fermentable. — Assamar is hygroscopic, deliquescent, soluble in *water* in all proportions, and not precipitable by *acids*, *alkalis*, *alkaline-earths*, *borax*, *tincture of galls*, or *isinglass*. It dissolves slowly and sparingly in cold, abundantly in boiling absolute *alcohol*, and is partially precipitated by ether. (Reichenbach, *Ann. Pharm.* 49, 1.) Pohl (*Wien. Akad. Ber.* 41, 623), having found that a purely bitter alcoholic extract of cane-sugar heated to 228°, acquired a sweet taste when dissolved in water and so preserved for some years, supposes assamar to be capable of regenerating glucose.

2. Cane-sugar subjected to *dry distillation*, froths up strongly at about 250° or 300°, after having been previously transformed into caramel, and yields at first a slightly sour, yellow-distillate; then a darker coloured, turbid distillate; and, at last, one which is viscid and strongly acid. When it is slowly heated, gases first make their appearance towards the end of the distillation, amounting to 12 or 18 p. c. of the sugar, while a vesicular, carbonaceous residue amounting to 32 or 34 p. c. remains. — Comp. also Cruikshank (*Scher. J.* 1, 637); Vauquelin (*Bull. Pharm.* 3, 49). — The *gas* which escapes at first is nearly pure carbonic acid; afterwards carbonic oxide and marsh-gas are mixed with it. (Völckel, *Ann. Pharm.* 86, 63). — The aqueous distillate (Völckel's *sugar-vinegar*) becomes clear on standing from the separation of a viscid oil. This yields, by fractional distillation, a very volatile, yellowish liquid, which contains aldehyde (*Ann. Pharm.* 87, 303), acetone, and acetic acid, and is followed if the distillation is continued, by a mixture of acid water and yellow oil, while a red-brown liquid (Völckel's *sugar-tar*) remains. — The *yellow oil*, distilled with water after addition of potash-ley, dried, and then rectified alone, yields, between 100° and 150°, a distillate which has a density of 1.005 at 15° and amounts to  $\frac{1}{15}$  of the whole quantity; this product is neutral, precipitates silver from ammoniacal nitrate of silver, and turns brown and is destroyed by contact with potash-ley. The remainder, which distils between 160° and 180°, contains chiefly furfural (x, 371) (of various kinds, according to Völckel), together with a small quantity of an oil which is unalterable by potash, and traces of oil of bitter almonds, recognisable by the smell. — Furfural can still be extracted

by ether from the *sugar-vinegar* freed from oil as far as possible by distillation; the *sugar-vinegar* leaves a residue of tar, produced by the decomposition of assamar-acetic acid, every time it is distilled, while a certain quantity of this substance and common acetic acid pass over. The *sugar-tar* contains products of decomposition, partly of the volatile oils, partly of assamar. If three-quarters of the crude *sugar-vinegar* are distilled off, the decomposition-products of the volatile oils removed by filtration, and the filtrate distilled, a large quantity of acid *sugar-vinegar* passes over below  $120^{\circ}$ , while a red-brown *sugar-tar* remains, which becomes viscid on cooling, has a strong, bitter, and sour taste, and amounts to 6 p. c. of the *sugar-vinegar*. Addition of water throws down a red-brown product of decomposition of assamar, whereof more is obtained by concentrating the filtrate and precipitating with water, while a bitter substance, Völckel's assamar, remains dissolved in the supernatant red-brown liquid.

Völckel's *Assamar*. The red-brown liquid obtained from *sugar-tar* is exactly neutralised with carbonate of soda, and evaporated on the water-bath to a syrup, whence assamar and other substances are extracted by boiling with absolute alcohol; and the cooled extract is precipitated by several volumes of ether, whereby acetate of soda and red-brown substances are precipitated. The ether-alcoholic solution, when distilled in the water-bath, leaves assamar behind as a brown syrup, which is purified by solution in ether, evaporation of the filtrate, solution in water, removal by filtration of the insoluble portion, and evaporation in vacuo. It is thus obtained as a yellowish-red transparent, viscid, neutral syrup, which does not solidify in vacuo, and contains on the average 54.70 p. c. carb., 5.40 hydr., and 39.90 oxyg. (Hence Völckel calculates the formula  $C^{20}H^{11}O^{11}$ , but one of the following formulæ appears more probable,  $5C^{24}H^{13}O^{13} + HO$  or  $C^{36}H^{20}O^{20}$ , the first of which requires the same percentage composition as Völckel's formula, and the second 54.54 p. c. carb., 5.05 hydr., and 40.41 oxyg. [Kr.]) According to Völckel, the substance is the same as Reichenbach's assamar before the latter has been altered and rendered solid by Reichenbach's method of preparation.—Assamar becomes more fluid when heated. It does not solidify even at  $120^{\circ}$  or  $140^{\circ}$ , so that its fluidity cannot be due to adhering water. Above  $200^{\circ}$  it is decomposed, with formation, of a solid substance.—By boiling with dilute *hydrochloric acid*, it is changed into a brown substance which is insoluble in water, and contains on an average 65.18 p. c. carb., 4.55 hydr., and 30.77 oxyg., corresponding therefore in composition to Mulder's ulmin from sugar and perhaps having the formula  $C^{24}H^{10}O^9$ ; traces of formic acid are produced at the same time as this substance. By treatment with potash-ley it is further split up into a soluble and an insoluble portion, each of which contains oxygen and hydrogen in the same proportion as water.—Assamar yields the same products by boiling with *potash-ley* as with acids. The red-brown alkaline solution, precipitated by hydrochloric acid after several hours' boiling, yields brown flocks, which, if covered with potash-ley, after being washed, partly dissolve and partly swell up to insoluble potash-compounds: freed from potash by hydrochloric acid, they contain 61.36 p. c. carb., 4.60 hydr., and 34.04 oxyg., corresponding to the formula  $C^{12}H^5O^5$  (calculation 61.53 p. c. carb., 4.27 hydr., and 34.20 oxyg.)—Assamar

colours aqueous *bichromate of potash* brown when boiled, and reduces ammoniacal *nitrate of silver* with the aid of heat.—It is hygroscopic, dissolves easily in *water*, and is precipitated from the solution by animal charcoal. It dissolves *hydrate of lime*, precipitates ammoniacal *sugar of lead*, and is easily soluble in *alcohol* and *ether*. (Völckel, *Ann. Pharm.* 85, 74).

3. When *oxygen* or *air*, especially ozonised air, is passed over dry or aqueous cane-sugar, carbonic acid and water are formed at the common temperature, the rest of the sugar remaining unchanged. A piece of cane-sugar (weighing 1 drachm) left in contact with oxygen confined by mercury for three months, produced 5 cc. carbonic acid in 95 cc. oxygen. (Karsten, *Berl. Akad. Ber.* Jan. 1860; abstr. *J. pr. Chem.* 79, 226.)—Aqueous solution of cane-sugar is not altered by ozone. (Gorup-Besanez, *Ann. Pharm.* 110, 103). If cane-sugar mixed with a little hydrate of lime is covered with a stratum of ozonised oil of turpentine and left for seven months, oxalic acid is formed, while the rest of the sugar remains unchanged. (Berthelot, *N. Ann. Chim. Phys.* 58, 426).

When *oxygen* is passed over a mixture of cane-sugar and spongy platinum, formation of carbonic acid and water commences at 140°—150°, and at 250° the sugar is completely decomposed. (Reiset & Millon, *N. Chim. Phys.* 8, 285; *J. pr. Chem.* 29, 365).—Cane-sugar mixed with spongy platinum is not affected by oxygen at the common temperature, but becomes heated on addition of potash, and is oxidised to carbonic acid and water. (Döbereiner, *J. pr. Chem.* 29, 452).

4. Cane-sugar swells up in the *open fire*, produces an aromatic, choking smell of caramel, and burns with a white flame.—In the combustion of large quantities of sugar, a powerful smell is produced allied to acrolein, which attacks the eyes and causes them to inflame. (Redtenbacher, *Ann. Pharm.* 47, 148).

5. Cane-sugar takes fire when triturated with 8 pts. *peroxide of lead*. (Böttger). Its aqueous solution yields formic and carbonic acids by boiling with peroxide of lead, but not so easily as glucose. (Stürenberg, *Ann. Pharm.* 29, 291.)—By distillation with *peroxide of manganese and sulphuric acid*, it yields formic acid and a strong-smelling yellow oil, heavier than water, which may be obtained pure by neutralising the distillate with a base, distilling off the volatile part, and rectifying over chloride of calcium; it is then found to be soluble in water. (Döbereiner, *Schw.* 63, 368). Comp. also Gmelin (*Pogg.* 16, 55). Peroxide of manganese does not act upon sugar without the addition of sulphuric acid. (Stürenberg.)—Formic acid is obtained by distilling it with *bichromate of potash* and moderately dilute sulphuric acid. (W. & R. Rogers; Hünefeld, *J. pr. Chem.* 7, 44.) When solution of cane-sugar is mixed with hot concentrated aqueous bichromate of potash and the mixture heated to boiling, a violent re-action sets in, which continues, even after removal of the lamp, until the solution has become green. If  $\frac{1}{8}$  or a larger quantity of starch-syrup is mixed with it, no re-action or change of colour occurs. (Reich, *J. pr. Chem.* 43, 72).

Dilute solution of cane-sugar precipitates peroxide of manganese from aqueous *permanganate of potash*, without evolution of gas, and forms oxalate of potash, which is converted by excess of perman-



ganate into carbonate of potash (Liebig & Pelouze, *Ann. Pharm.* 19, 279; Gregory & Demarçay). If the solution contains only 0.5 — 1 p. c. sugar it remains unchanged (Monier, *Compt. rend.* 46, 577).

If 3 pts. dry chloride of lime are added to a mixture of 2 pts. cane-sugar and 1 pt. hydrate of lime, and then enough water to form a stiff mud, the mass becomes heated after some time, swells up, evolves chlorine, and on addition of more water, forms a bulky jelly, which, in addition to substances not yet determined, contains lime-compounds of hypochlorous, carbonic, chloracetic and pectic (? Kr.) acids. — When twice as much chloride of lime is used, the re-action is less violent and malic acid is produced. (Schoonbrodt, *Bull. Soc. Chim. Paris*, 1861, 77.) Schoonbrodt gives the following equations: *a*, for the formation of pectic (or parapectic) acid,  $-2C^2H^{10}O^{11} + 3(CaO, ClO) = C^2H^{15}O^{21}, 2HO + 3CaCl + 5HO$ ; — *b*, for the formation of malic acid,  $-C^2H^{10}O^{11} + 3(CaO, ClO) = 3(C^2H^3O^4, HO) + 2HO + 3CaCl$ .

6. Cane-sugar distilled with *sulphur* evolves sulphuretted hydrogen, combustible gases, and allows a metacetone-like liquid to distil. (Eilasiwetz, *Wien. Akad. Ber.* 5, 184.) Similar products are obtained with sulphide of potassium or of calcium.

7. *Iodine* is decolorised by ebullition with solution of cane-sugar and transformed into hydriodic acid. (Lassaigne, *J. Chim. méd.* 9, 654.) — When equal numbers of atoms of bicarbonate of potash and of iodine are added one after another to aqueous cane-sugar, iodoform is produced on warming. (Millon, *Compt. rend.* 21, 828; *J. pr. Chem.* 37, 53.) — Cane-sugar is decomposed exactly into carbonic acid and water when heated with aqueous *iodic acid* to  $100^\circ$  for 24 hours. The presence of prussic acid, but not that of yellow or red prussiate of potash, prevents this decomposition. (Millon, *Compt. rend.* 19, 271; *N. Ann. Chim. Phys.* 13, 37.)

7a. *Bromine* acts on cane-sugar in the same way as chlorine (Rouchas, *J. Pharm.* 17, 116); it exerts no particular action. (Balard, *Ann. Phys.* 32, 346.) Cane-sugar heated with *bromine* and water to  $100^\circ$  in a sealed tube, till all the bromine has disappeared, yields hydrobromic acid, a brown liquid and humus-like products. (Barth & Eilasiwetz.)

8. Dry *chlorine* gas does not act on cane-sugar, even at  $100^\circ$ ; but in damp chlorine, sugar acquires a smell of hydrochloric ether without altering its form. (Liebig.) Powdered sugar absorbs chlorine slowly, and is changed, with simultaneous formation of carbonic acid, into a brown, strong-smelling mass, which deliquesces in the air with formation of hydrochloric acid. (Priestley, Bouillon, Vogél.) — The brown mass into which chlorine slowly converts sugar in the cold, more quickly at  $100^\circ$ , is partially soluble in water. (Maumené, *Compt. rend.* 30, 314.) — By the action of chlorine on an aqueous solution of sugar for eight hours,  $\frac{1}{6}$ th part, at most, is decomposed, with formation of carbonic acid (Liebig, *Pogg.* 15, 570). Aqueous chlorine converts sugar into malic and hydrochloric acids (Chenevix), into the same acid as that which is likewise produced from gum (p. 199) (Simouin, *Ann. Chim. Phys.* 50, 322). — Solution of cane-sugar saturated with chlorine, and heated with potash after 24 hours, is coloured yellow and red. (Rouchas, *J. Pharm.* 17, 116.) — With *hypochlorous acid*, sugar forms hydrochloric acid, a small quantity of carbonic acid, and an acid liquid. (Balard.) — Cane-sugar, mixed with its own weight of *chloride*

of lime, becomes heated and explodes after a few minutes with vivid deflagration. If 1 oz. chloride of lime is mixed with 8 oz. water, and 1 oz. sugar is added to the filtrate, the liquid becomes hot, and, after a few minutes, carbonic acid is evolved, the bleaching power disappears, and the acid liquid deposits a little oxalate of lime. (Hunoult-Desfontenelles, *J. Chim. méd.* 18, 23.) No chloroform is thus produced. (Chautard, *N. J. Pharm.* 27, 180.) — Chloride of lime converts sugar in an alkaline solution into pectic and lactic acids. (Schoonbrodt, *Compt. rend.* 52, 1071.) Concentrated solution of cane-sugar becomes heated when mixed with 1 pt. chloride of lime and 3 pts. water, and yields formic acid if the chloride of lime was neutral; carbonic acid and water, if it contained excess of hydrate of lime. (Bastick, *N. J. Pharm.* 14, 20.) See page 252.

9. Canc-sugar does not absorb gaseous *fluoride of boron* until it is heated, and it then becomes black. (Berthelot, *N. Ann. Chim. Phys.* 38, 58.)

10. The solution of cane-sugar in water partially loses its dextro-rotatory power at the common temperature by standing; at last, it loses it entirely, and acquires a rotatory power towards the left, the cane-sugar being converted into inverse sugar. (Maumené.) According to Hochstetter, this change does not occur if air is excluded, but more quickly in proportion as the air has freer access; according to Béchamp, it is only a consequence of the formation of mould, and is therefore prevented by the presence of creosote. Aqueous solution of sugar may be kept for weeks without alteration if protected from the air, but if exposed to the air, it contains, after 3 days' traces of inverse sugar which afterwards increase. When the air has easy excess, as when the sugar-solution flows over broken glass, scarcely anything but non-crystallisable sugar remains after so short a time as 36 hours (Hochstetter, *J. pr. Chem.* 29, 21). An aqueous solution of sugar-candy containing 16·35 grms. sugar in 100 cc. possesses, after standing for 10 months at the common temperature, only 22 p. c. of its original rotatory power; after a year, it has a lævo-rotatory power equal to 38 p. c. of its original dextro-rotatory power. A similar solution prepared with loaf-sugar is somewhat more stable, because it contains a small quantity of lime. (Maumené, *Compt. rend.* 39, 914).

Cane-sugar is converted by very long boiling with water into dextro- and lævo-glucose. (Pelouze & Malaguti, 1836, *Ann. Chim. Phys.* 59, 416). According to Malaguti, lævo-glucose (fruit-sugar) is thus produced at first, and afterwards changed into dextro-glucose; according to Bouchardat, dextro-glucose is never formed, but, after 60 hours' boiling, a non-crystallisable syrup, which can then, especially at 110°, pass into a peculiar bitter-sweet gum-sugar. According to Dubrunfaut's experiments (*Vid. infr.*, p. 254. — Decompositions by acids.), the formation of dextro- and lævo-glucose unquestionably occurs simultaneously, as is also admitted by Maumené and Béchamp. — This transformation of cane-sugar takes place at 90°—100° (Thénard), if air is excluded, without the formation of acid or of colouring matter (Soubeiran), but the passage of air through the boiling solution of sugar causes rapid decomposition. (Hochstetter.) Solution of sugar of 25° B. boiled for 1 or 2 hours, the evaporated water being replaced, contained traces of transformed sugar, perhaps arising from previous formation of formic acid. The transformation once begun proceeds rapidly, an acid being formed

which does not redden litmus, though it neutralises alkalis. (Hochstetter, *J. pr. Chem.* 29, 21.) — Solution of sugar-candy lost from  $3\frac{1}{2}$  to 4 p. c. of its rotatory power when heated for 3 hours in the water-bath. (Maumené, *Compt. rend.* 39, 914). If solution of sugar is boiled, the water which evaporates being replaced, its dextro-rotatory power becomes weaker and weaker, and is at last quite lost. At this point, and until the subsequent lævo-rotatory power has not arrived at its maximum, the liquid still contains unaltered cane-sugar, for addition of acids still increases the lævo-rotation. When the transformation is complete, for which 114 hours' boiling is necessary, longer boiling causes the formation of formic and acetic acids and (even in a stream of carbonic acid) a dark coloration; at last the liquid becomes opaque, and the lævo-rotation diminishes again, from the partial destruction of the lævo-glucose, so that it has finally a feeble dextro-rotatory power. The lævo-rotatory liquid deposits crystals of dextro-glucose when allowed to stand, while a syrup of stronger lævo-rotatory power remains. (Soubeiran, *N. J. Pharm.* 1, 1; and 96, 16 and 262.)

11. When left to itself, or when warmed with *dilute acids*, solution of cane-sugar loses its dextro-rotatory power and acquires a lævo-rotatory power, which, when the transformation (*Inversion*) is complete, amounts to  $38^\circ$  to the left at  $14^\circ$  for every  $100^\circ$  of the original rotation to the right (Biot). This alteration depends on the assimilation by the cane-sugar of 5 p. c. water, whereby it splits up into lævo- and dextro-glucose:  $C^{12}H^{22}O^{11} + 2H^1O = C^{12}H^{12}O^{12} + C^{12}H^{10}O^{12}$  (Dubrunfaut). (Water taken up: calculated, 5.26 p. c.).

There is produced in the transformation of cane-sugar by dilute acids, grape-sugar (Kirchhoff, *Scher. N. Bl.* 1, 142), granular sugar (Guibourt, *Ann. Chim. Phys.* 16, 376; Boullay, *J. Pharm.* 16, 172), gum-sugar (Bouillon-Lagrange). A sugar differing from dextro-glucose is produced which rotates the plane of polarisation to the left (Biot), and afterwards, in consequence of a molecular change, deposits dextro-glucose (Biot, Soubeiran). Cane-sugar heated with acids forms first lævo-glucose, then, if the heat is continued, dextro-glucose (Bouchardat); but since boiling with acids does not alter the rotatory power of inverse sugar until coloration takes place, the crystals of dextro-glucose which are deposited after some months, may be produced, not by the action of the acid, but by the molecular transformation which takes place in the course of time (Soubeiran). Subsequently, also, Soubeiran regarded inverse sugar as a particular variety, but capable of being decomposed into dextro- and lævo-glucose.

All acids effect the complete conversion of cane-sugar, but strong acids more quickly than the same quantity of weaker acids, and the same acid acts more rapidly the higher the temperature. The change is complete with  $\frac{1}{16} - \frac{1}{11}$  measure hydrochloric acid at the temperature of the air in a few hours, the rotatory power then possessed by the liquid remaining constant for two days, or until coloration sets in. With sulphuric acid the transformation takes place slowly at the common temperature, but at  $60^\circ$  or  $70^\circ$  instantaneously and without coloration of the liquid. A solution of cane-sugar containing 66 p. c. racemic acid, is only partially changed after sixteen days, completely after a year;  $\frac{1}{4}$  measure glacial acetic acid does not occasion the transformation within two months, but completely within a year (Biot, *Compt. rend.* 15, 528; *N. J. Pharm.* 4, 351). Small quantities of organic

acids do not sensibly increase the decomposing action of water at common temperatures (p. 253). A 30 p. c. solution of cane-sugar mixed with  $\frac{1}{10}$  of its weight of tartaric acid was not completely converted into inverse sugar after 5 years. (Maumené, *Compt. rend.* 39, 917). The cane-sugar of lemon-juice (containing  $6\frac{1}{2}$  p. c. acid) is only very slightly changed after 12 days, not more so than when the free acid is neutralised. The acid juice of the apricot may likewise be concentrated on the water-bath to half its bulk without the inversion of much of its cane-sugar (Buignet). If solutions of cane-sugar are heated with solutions of equivalent quantities of different acids, sulphuric acid causes its inversion more quickly than tartaric acid, and tartaric acid more quickly than citric or than acetic acid. A larger quantity of the same acid is required if the sugar-solution is dilute than if it is concentrated (Buignet). See also Persoz (*Compt. rend.* 17, 1066), Biot, *N. J. Pharm.* 4, 351, Bouchardat (*J. Pharm.* 21, 627; *J. pr. Chem.* 7, 73; *Ann. Pharm.* 17, 276), Döbereiner (*Ann. Pharm.* 2, 338); Mitscherlich (*N. Ann. Chim. Phys.* 7, 28), Pluquet (*Bull. Pharm.* 3, 380).

When the transformation of cane-sugar by dilute acids has taken place, further boiling causes coloration of the liquid, formation of ulmin and ulmic acid, and, if air has access, also of formic acid, while the remainder of the sugar is contained in the solution in a more easily fermentable condition (Malaguti). According to Mulder, glucic acid is first formed, from this apoglucic acid, by contact with air, and ulmin and ulmic acid, mixed, if air has access, with humin and humic acid, are obtained. The acid which is added remains thereby unaltered and can be regained in the quantity that was used (Malaguti).

The decomposition takes place with all acids, but various quantities are required to bring it about in the same length of time. The solution of 100 pts. sugar in 300 pts. water begins to deposit a precipitate after 35 hours' boiling, if mixed with 0.372 pt. anhydrous sulphuric acid; after 14 hours with 2.4 pts; after 9 hours with 6 pts; after 2 hours with 14.7 pts. Nitric and hydrochloric acids act in the same way; for every 1 pt. of these acids, 10 pts. oxalic, racemic, tartaric, citric, or saccharic acid—and 16 pts. phosphoric, arsenic, phosphorous, or arsenious acid,—are required. (Malaguti, *Ann. Chim. Phys.* 59, 407; *J. Pharm.* 21, 443; *Ann. Pharm.* 17, 52; *J. pr. Chem.* 7, 185.)

On heating 50 pts. water, 1 to 5 pts. oil of vitriol, and 10 to 20 pts. cane-sugar for a few minutes in a water-bath, a deposit of ulmic acid is formed (Bouchardat). Transformed cane-sugar, heated with  $\frac{1}{2}$  pt. oil of vitriol, yields, after a few minutes' boiling, a brown liquid, which leaves bitter-sweet molasses by evaporation, cannot be decolorised by animal charcoal, and is uncrystallisable (Bouchardat). Solution of cane-sugar does not lose the rotatory power peculiar to inverse sugar until boiled for 15 or 20 hours with dilute sulphuric acid, and then deposits much less ulmin in the first few days than later. If it be boiled with a small quantity of acid until a deposit forms, and this be filtered off, a large quantity of ulmic acid separates in the cold after a long time, but no ulmin; the latter body must therefore be formed from the ulmic acid by boiling. By 84 hours' boiling of 40 grms. sugar-candy with 120 grms. water and 2 grms. anhydrous sulphuric acid, 13 grms. ulmin and ulmic acid, and, in contact with air, 4.47 grms. formic acid can be obtained, while all the rest of the sugar remains in solution in a more easily fermentable condition (Malaguti). If

solution of cane-sugar is heated with dilute sulphuric acid, but not to boiling, ulmin and ulmic acids are obtained, mixed, if the solution is boiled, with humin and humic acid. These humous substances are formed more quickly if air has free access; concentration of the acid promotes their formation less than long boiling; but on an average, not more than  $\frac{1}{5}$  of the sugar can be converted into them, the rest remaining in solution as glucic acid (xiii. 237), and if air has access, also as apoglucic acid (xiii. 365). If the action of the acid is not complete, uncrystallisable sugar remains behind, and is converted by dilute, not by concentrated acid, into humin. The humous substances are not produced at the boiling point in vacuo: if very concentrated acid is used, a black substance is obtained having the composition of humin, but differing from it. By the use of more dilute acid, nothing but glucic acid is obtained. At the higher temperature at which the mixture boils in air free from oxygen, formic and ulmic acids are produced, but neither humin nor humic acid (Mulder, *J. pr. Chem.* 21, 207).

If cane-sugar is heated, not to boiling, with hydrochloric acid, the red-brown liquid deposits a few brown flocks. If it is heated to boiling after these have been filtered off, a more abundant black precipitate is obtained, which is slightly soluble in boiling water, more so in water containing hydrochloric acid, partially soluble in aqueous potash and ammonia. The brown flocks contain 62.54 p. c. C. and 4.75 H.; the black precipitate at  $140^{\circ}$ , on an average, 64.12 p. c. C. and 4.71 H., corresponding to the formula  $C^{24}H^9O^9$  (calculation 64.0 p. c. C., 4.0 H.). The latter body is also obtained by boiling sugar with concentrated hydrochloric acid (Stein, *Ann. Pharm.* 30, 84).

12. By *neutral salts*. Aqueous solutions of cane-sugar mixed with sulphate of zinc, nitrate of lead, mono-phosphate or arseniate of potash, or with a large quantity of corrosive sublimate, lose their dextro-rotatory power partially or entirely by standing at the temperature of the air, and occasionally acquire a rotation towards the left, without the formation of mould taking place. Corrosive sublimate causes this transformation even in presence of creosote. On the other hand a solution of cane-sugar containing  $\frac{1}{4}$  of its weight of fused chloride of zinc (or of chloride of calcium) hardly decreases in rotatory power by standing for 9 months, or when heated for an hour to  $50^{\circ}$ . The presence of a small quantity of corrosive sublimate, nitrate of zinc, neutral or acid sulphate of potash, prevents the formation of mould in solutions of cane-sugar, and consequently also the decomposition. Most other salts, and likewise nitric and arsenic acids, do not prevent the formation of mould, and in many cases the decomposition of solution of cane-sugar goes on more rapidly in their presence than without them. If solutions of cane-sugar are mixed with neutral and acid sulphate of soda and one drop of creosote, no formation of mould or decomposition takes place by standing, but creosote has not power to arrest the formation of mould when it has once begun. In the case of some salts, a summer temperature seems to be required for the decomposition; nitrogenous mould and organic acids result from the decomposition itself, but the latter are not formed in such quantity that the diminished rotatory power of the solution can be explained by the diminution of the quantity of sugar. (Béchamp, *N. Ann. Chim. Phys.* 54, 28.)

Sugar-solutions which contain alkaline carbonates, sulphates, or

chlorides, behave like pure solutions of sugar, when long kept or boiled, but the crystallisation of the sugar is impeded. A solution containing 2 pts. chloride of sodium or chloride of calcium to 100 pts. cane-sugar cannot be made to crystallise except when the salts have been removed by animal charcoal. Alkaline nitrates and sulphates partly crystallise out from the solution of sugar when they are present in large quantities, but part forms a slimy mass with the sugar (Hochstetter, *J. pr. Chem.* 29, 26).

Dry cane-sugar is not altered by being heated in a sealed tube to 100° for several hours with *chloride of sodium, chloride of strontium, or chloride of barium*; but addition of a small quantity of water occasions the formation of inverse sugar more abundantly than it would be formed in presence of water alone. The same transformation takes place quickly, the mass being blackened, with sal-ammoniac and a small quantity of water, but not with chloride of potassium, chloride of sodium, or flour-spar. (Berthelot, *N. Ann Chim. Phys.* 38, 57.)

13. Cane-sugar distilled with *phosphoric acid* (likewise with sulphuric acid or protochloride of tin) yields formic acid and a volatile oil (furfural?) (Emmet *J. pr. Chem.* 12, 120). — Anhydrous phosphoric acid does not attack cane-sugar until heat is applied; it then blackens it, with evolution of formic acid and formation of humus-like bodies. (Ifandtke, *Pharm. Zeitschr.* 1850, 37; *Lieb. Kopp. Jahresber.* 1850, 534.)

14. Cane-sugar covered with cold *oil of vitriol* becomes brown without evolving sulphurous acid; the mixture is completely soluble in water without separation of carbon, and, after neutralisation of the sulphuric acid with chalk, filtration, and evaporation to dryness, yields a dark brown residue containing sulphur. (Braconnot, *Ann. Chim. Phys.* 12, 189.) Oil of vitriol produces with cane-sugar the same black acid as that formed from racemic acid by alkalis and also saccharo-sulphuric acid, or a similar compound. (Peligot.) If the process is arrested at the right moment, humous substance is also formed. (Boullay.) The filtrate obtained by mixing cane-sugar with oil of vitriol, dilution, and neutralisation with baryta, contains acetate and formiate of baryta. (Herzog, *N. Br. Arch.* 50, 299.) If a porcelain plate is moistened with a solution of sugar in 30 pts. water, and heated by steam to 100°; very dilute sulphuric acid dropped upon it causes a black mark, or, if the acid is very dilute indeed, a green mark. (Runge, *Pogg.* 31, 517.) Runge employs this re-action for the detection of free sulphuric acid and of sugar.

When cane-sugar is heated with oil of vitriol, sulphurous acid is produced. 10 grms. cane-sugar warmed with 40 grms. oil of vitriol froths up, blackens and yields 1 litre of gas, containing carbonic acid and carbonic oxide in equal volumes, and a solid residue. (Filhol, *N. J. Pharm.* 8, 100; *J. pr. Chem.* 36, 60.)

15. Concentrated *hydrochloric acid* acts violently on cane-sugar and chars it. (Boullay, *J. Pharm.* 16, 172.) Powdered sugar slowly absorbs hydrochloric acid gas, and is converted into a brown strongly smelling compound from which oil of vitriol evolves hydrochloric acid gas. (Bouillon-Lagrange.)

16. Cane-sugar mixed with *chlorate of potash* explodes when struck

with a hammer, and deflagrates when a drop of oil of vitriol is let fall upon it. (Bouillon-Lagrange & Vügel.)—A mixture of 1 pt. cane-sugar, 1 pt. prussiate of potash, and 2 pts. chlorate of potash (Augendre, *Pharm. Centr.* 1850, 215), or better of 23 pts. cane-sugar, 28 pts. prussiate of potash, and 49 pts. chlorate of potash, constitutes white gunpowder, which explodes by a spark, and may be used instead of common gunpowder for fire arms and blasting. (Pohl, *Wien. Akad. Ber.* 41, 634; *Chem. Centr.* 1861, 289.)

17. Fuming nitric acid converts cane-sugar into nitro-saccharose. (Sobrero, *Compt. rend.* 24, 247.) From its solution in fuming nitric acid it is precipitated as a nitro-compound by oil of vitriol, but not by water. (Domonte & Ménard, *Compt. rend.* 24, 390.) Hence also Braconnot obtained no xyloidin. — Immersed in nitro-sulphuric acid, it is converted into nitro-saccharose, which soon separates as a tough mass, while the acid solution, which is not precipitable by water, retains a bitter taste. (Schönbein, *Pogg.* 70, 104.) On adding to nitric acid (prepared from 3 vol. oil of vitriol and 2 vol. nitric acid of sp. gr. 1.5,  $\frac{1}{2}$  of its weight or more of powdered sugar, without cooling, and leaving the mixture to itself, it took fire. (Reinsch, *Jahrb. pr. Pharm.* 18, 102.)

Cane-sugar heated with nitric acid of sp. gr. 1.3, or with still more dilute acid, is decomposed, with evolution of nitrogen, nitric oxide, nitrous acid, prussic acid, carbonic and acetic acids, and formation of saccharic and oxalic acids. According to Erdmann's experiments, tartaric acid is also formed, and according to Siewert, also cassonic acid (see p. 259). — When 8 pts. nitric acid are poured upon 1 pt. cane-sugar at  $33\frac{3}{4}^{\circ}$ , the liquid around the sugar becomes red in a few minutes, at  $15^{\circ}$  it becomes pale yellow, and at  $44^{\circ}$  the sugar deliquesces to a yellow layer under the clear colourless acid. At  $56^{\circ}$  the liquid becomes yellow and evolves nitrous acid; it darkens as the heat is increased, until, at  $87.5^{\circ}$ , it is opaque, and then, with evolution of nitrous acid, again becomes colourless. The temperature of a mixture heated to this point rises spontaneously to  $112.5^{\circ}$ . (Schlesinger, *Repert.* 74, 24.)

By the action of 3 pts. nitric acid of sp. gr. 1.25 to 1.3, at a temperature not exceeding  $50^{\circ}$ , scarcely a trace of oxalic acid, but a large quantity of saccharic acid is produced. Cane-sugar heated with  $3\frac{1}{2}$  pts. nitric acid, until gas begins to be given off, then cooled to  $60^{\circ}$  and kept at this temperature, yields nearly 11 p. c. of its weight of neutral saccharate of potash. (Heintz, *Ann. Pharm.* 51, 185. — *Berl. Akad. Ber.* 1858, 413; *J. pr. Chem.* 74, 474.) Formerly (*Ann. Pharm.* 21, 1.) Erdmann stated that he had obtained tartaric acid, but afterwards (*J. pr. Chem.* 15, 480) withdrew the statement. Since, however, Liebig (*Ann. Pharm.* 113, 1), has obtained tartaric acid from mannite, and Heintz (*Berl. Akad. Ber.* 1860, 283) has obtained it from saccharic acid, the statement appears nevertheless to be correct. See also milk-sugar p. 220, and saccharic acid, xi. 516. — Oxalic acid is formed especially when sugar is heated for a long time with excess of nitric acid. If cane-sugar is boiled with increasing quantities of nitric acid of sp. gr. 1.38 and each portion is evaporated to the same bulk, a colourless syrup, which becomes coloured on heating, is obtained with 2 pts nitric acid; the same mixed with crystals of oxalic acid is obtained with 4 pts. acid; with 10 or 12 pts. acid, nothing but crystals of oxalic acid, amounting to 58 or 60 p. c. of the sugar, and without any sticky mother-ley, are obtained. (Schlesinger, *Repert.* 74, 27.) — The dark

mother-ley, which remains after separating the oxalic and saccharic acids formed by treating cane-sugar with commercial nitric acid, contains *cassonic acid*, which may be precipitated by sugar of lead. This compound, when separated from its lead-salt, forms an uncrystallisable, reddish syrup, whose aqueous solution produces a metallic mirror with ammoniacal nitrate of silver, is precipitated by excess of baryta-water, and when mixed with ammonia and chloride of barium throws down white flocks of cassonate of baryta, containing  $C^{10}H^6Ba^2O^{14}$ . (Siewert *Zeitschr. f. d. ges. Naturw.* 14, 337; abstr. *Kopp's Jahresber.* 1859, 548.)

18. In contact with moist or aqueous *arsenic acid*, cane-sugar deliquesces in a few hours, even in the dark and when air is excluded, to a syrup which is red at first, but after 14 days becomes red-brown, and at last black-brown and evolves a smell of acetic acid. Part of the arsenic acid is thus converted into arsenious acid and part of the sugar into glucose. (Elsner, *Schw.* 50, 348.—61, 230.) The reduction of the arsenic acid is not essential; on the one hand, humus seems to be produced by the elimination of water, and, on the other hand, glucose by its fixation. (Schweigger-Seidel, *Schw.* 61, 356.) The red colour is due to the formation of humus. (Malaguti.) A dry mixture of sugar and arsenic acid deliquesces in dry air over hydrate of lime to a red mass, which becomes black after a few days. (Rouchas, *J. Pharm.* 17, 116.) The red solution gives a rust-coloured precipitate with lime-water. (Baumann, *N. Br. Arch.* 37, 47.) A solution containing  $\frac{1}{10}$  pt. cane-sugar heated in steam for a few seconds with a 1 p. c. solution of arsenic acid, becomes red at the margin, and on evaporation leaves a bright red spot. (Elsner, *Pogg.* 47, 481.) Arsenic acid added to solution of cane-sugar does not prevent the formation of mould and the consequent decomposition of the sugar on standing; arsenic acid and creosote together only prevent the decomposition from beginning, they do not arrest it when once begun. (Béchamp.) See also p. 256.

19. Cane-sugar heated for some time with aqueous *osmic acid* evolves carbonic acid, and forms oxalic acid and a peculiar acid whose ammonia-salt is soluble in alcohol. (Buttlerow, *J. pr. Chem.* 56, 274.) — Cane-sugar reduces *vanadic acid* to vanadic oxide. (Berzelius.)

20. A mixture of cane-sugar and *oxalic acid* moistened with water, deliquesces in the water-bath, to a colourless syrup, which afterwards becomes brown and lastly black-brown, and yields to water fruit-sugar and glucose, while a black residue remains, containing 61.87 p. c. carb., 4.48 hydr., and 33.65 oxyg., answering to the formula  $C^{24}H^{10}O^{10}$  (calculation: 61.54 p. c. carb., 4.27 hydr.) and resembling Mulder's humin [more closely, Maumenés caramelin (p. 262) (Knop, *Chem. Centr.* 1856, 847)]. A little carbonic acid escapes at the same time, and formic acid, produced by the decomposition of oxalic acid, not of the sugar, passes over with the aqueous vapour (together with oxalic acid). (Van Kerckhoff, *J. pr. Chem.* 69, 48) See also Döbereiner (*Ann. Pharm.* 2, 338).

21. Cane-sugar heated to 100° or 120° with *acetic*, *butyric*, *benzoic*, or *stearic acid*, yields, with elimination of water, products resembling those obtained from glucose under the same circumstances. *Tartaric*



acid heated with 1 at. cane-sugar gives Berthelot's *acide glucoso-ditartrique*. (Berthelot, *N. Ann. Chim. Phys.* 54, 78. — 60, 93; *Chim. organ.* 2, 257, 271 and 295.) A mixture of cane-sugar and *succinic acid* in atomic proportions melts to a dark brown syrup at  $120^{\circ}$  —  $130^{\circ}$ , and yields a compound of succinic acid with glucose, water being set free. (van Bemmelen, *Kopp's Jahresber.* 1858, 436.) We ought perhaps, with Berthelot (*Chim. organ.* 2, 295), to regard these compounds as mixtures containing succinic acid combined, partly with lævo-glucose sugar, and partly with dextro-glucose. [Kr.]

22. When *ammonia gas* is passed over cane-sugar which is heated above  $150^{\circ}$ , but not so strongly as to decompose it, water and carbonate of ammonia escape, while liquid and insoluble substances remain in the residue, containing 10 p. c. of nitrogen not removable by aqueous alkalis. These bodies are not formed at  $130^{\circ}$ . (P. Thenard.) Cane-sugar behaves like starch (p. 87) when heated with aqueous ammonia. (Schützenberger, *Zeitschr. Ch. Pharm.* 4, 65.) See also Schoonbrodt (*Compt. rend.* 52, 1071) who states that he obtained from sugar, by the action of ammonia with the aid of phosphoric acid, a product containing  $C^{24}N^3H^{18}O^9$ .

By heating equal parts of cane-sugar syrup and aqueous ammonia in sealed tubes to  $180^{\circ}$  for 38 or 40 hours, a soluble and an insoluble black substance are obtained. The latter can be further decomposed, so that altogether four black or brown bodies are formed. Among them is a product soluble in alcohol, insoluble in water, containing 65.66 p. c. carb., 6.05 hydr. 19.36 nitr., and 8.93 oxyg., according to Thenard,  $C^{48}N^6H^{24}O^5$ . Another product, which is insoluble in water and in alcohol, but soluble in acids, contains 54.26 p. c. carb., 8.34 hydr., 18.78 nitr., and 21.62 oxyg.; Thenard assigns to it the formula  $C^{54}N^8H^{32}O^{16}$ . (P. Thenard. *Bull. Soc. Chim. Paris*, 1861, 18 and 33; abstr. *Compt. rend.* 52, 444; *Rép. Chim. pure*, 3, 207.)

23. Cane-sugar heated with *potassium* or *sodium* is decomposed with faint evolution of light, into charcoal and alkali. (Gay-Lussac & Thénard.)

A mixture of cane-sugar with 4 or 5 pts. *potash-hydrate* and a small quantity of water, becomes at first brown when heated, but is afterwards decolorised, evolves hydrogen, and then contains a large quantity of oxalate of potash. (Gay-Lussac, *Ann. Chim. Phys.* 41, 398; *Pogg.* 17, 171; *Schw.* 58, 87.) 100 pts. cane-sugar yield 32.1 pts. oxalate of lead. (Buchner & Herberger, *Repert.* 38, 189.) — If cane-sugar is added to hot concentrated *potash-ley* (such as would solidify on cooling) to the extent of  $\frac{1}{2}$  the weight of the potash-hydrate, the mass becomes brown, evolves hydrogen, gives off an aromatic smell of caramel, becomes thick after a few minutes, froths up until the brown colour has disappeared, and solidifies. The mass yields, on distillation with dilute sulphuric acid, carbonic acid, formic, acetic, and metacetic acids, and deposits binoxalate of potash. The sugar is in this case decomposed into carbonic acid, acetone and metacetone, the last of which yields propionic acid, while the acetone yields formic and acetic acids. Both are at last partially converted into oxalic acid. (Gottlieb, *Ann. Pharm.* 52, 122.)

Cane-sugar does not become sensibly brown when boiled with *potash-ley*. (Boullay, *J. Pharm.* 16, 172. — Chevalier, *J. Chim. méd.* 18, 471.) Solution of sugar heated with potash-ley to  $88^{\circ}$  and then neutralised with acid does not regain the whole of its rotatory power,

which is still further diminished when it is boiled or evaporated down. (Michaelis, *J. pr. Chem.* 56, 423.)—When cane-sugar is boiled for a long time with a small quantity of potash, out of contact with air, the potash becomes saturated with ulmic acid; if air has access, formic acid is also produced. (Malaguti, *Ann. Chim. Phys.* 59, 420.)—Carbonate of potash does not diminish the rotatory power of sugar when heated to  $88^{\circ}$ , but when boiled it does so to a less extent than caustic potash. (Michaelis.) By boiling solution of cane-sugar for 72 hours with  $\frac{1}{10}$  pt. crystallised carbonate of soda, an acid black liquid is formed possessing lævo-rotatory power. (Soubeiran.)

When a mixture of cane-sugar and inverse sugar is boiled for a few moments with caustic potash, the mass becomes coloured brown and black. After saturation with carbonic acid, basic acetate of lead precipitates from it nearly all the colouring matter, but no crystals can be obtained from the slightly-coloured solution which contains the whole of the cane-sugar, no doubt because the products of decomposition of the inverse-sugar prevent the crystallisation (Buignet).

24. Solutions of cane-sugar mixed with *hydrate of lime* exhibit greater stability when boiled or long kept than pure aqueous sugar-solutions (Boucharlat, Soubeiran, and others. *Comp.* p. 253). Hence the following observations are perhaps to be explained by the impurity of the sugar employed. When the compound of lime with cane-sugar is dissolved in a small quantity of water and exposed to the air, the lime separates out as carbonate, and the liquid changes to a white, tasteless paste, soluble in boiling water. This solution does not colour iodine, gives a slight turbidity with oxalic acid, and is precipitated by acetate of lead, bichloride of tin, and alcohol. It leaves on evaporation a solid brown mass which retains its solubility in water (Daniell, *Ann. Chim. Phys.* 10, 221). Braconnot found in aqueous sucrate of lime which had been kept for four years, a deposit of oxalate and malate of lime, and in the solution acetate of lime and cane-sugar, but no gum (*Ann. Chim. Phys.* 68, 337).—If a solution of cane-sugar supersaturated with lime is allowed to stand for a year in an air-tight bottle, the excess of lime contains neither oxalic nor malic acid. After removing the dissolved lime, evaporating and redissolving in alcohol, cane-sugar crystallises out, while melassic acid, saccharic acid, and uncrystallisable sugar remain in the mother-liquor (Brendecke, *N. Dr. Arch.* 29, 75; see also Berthelot p. 251).

When an intimate mixture of 1 pt. cane-sugar and 8 pts. *quick-lime* is heated, a violent re-action takes place, as the sugar gives up water to the lime, continuing even after the mixture is removed from the fire; no gas is evolved, but a brown, oily mixture of acetone and metacetone passes over. (Freymy, *Ann. Chim. Phys.* 59, 5.) The same products are obtained in greater abundance with 3 pts. lime to 1 pt. sugar. (Gottlieb, *Ann. Pharm.* 59, 5.)—When cane-sugar is distilled with *soda-lime*, small quantities of ethylene, propylene, and amylene are obtained. (Berthelot, *Inst.* 1857, 269; *Kopp's Jahresber.* 1857, 426.)

When considerable quantities of cane-sugar are heated with 3 to 8 pts. *quick-lime*, combustible gases are evolved, and a liquid distillate passes over, containing acetone, oils of the formulæ  $C^{14}H^{11}O^3$ ,  $C^{16}H^{13}O^3$ ,  $C^{20}H^{17}O^3$ , and  $C^{28}H^{25}O^3$ , a small quantity of resin, and substances soluble in potash-ley. (R. Schwarz.)

When the liquid distillate is rectified with water, the resin remains behind, while a pale yellow oil floats on the water which passes over. On agitating this resin with milk of lime, and distilling the filtrate with dilute sulphuric acid, acetic and propionic acids pass over.

The pale yellow oil gives up acetone to water; the insoluble portion is partly dissolved, with dark red-brown colour, by potash-ley, the oil which floats on the surface acquiring at the same time an agreeable odour. The potash-solution, distilled with sulphuric acid, deposits resin and gives off traces of fatty acids, together with a neutral oil having an odour of peppermint, containing 61.07 p. c. carbon, 12.10 hydrogen, and 26.83 oxygen, and agreeing, according to Schwarz, with the formula  $C^8H^7O^3$ .

The portion of the pale-yellow oil which has been treated with water and potash-ley, if again subjected to fractional distillation, passes over between  $70^\circ$  and  $250^\circ$ , but not completely. The portion volatilised at  $70^\circ$  contains 70.30 p. c. C., 9.52 H., and 20.18 O., according to Schwarz =  $C^{14}H^{11}O^3$ ; that which volatilises at  $95^\circ$  contains 73.72 C., 10.25 H., and 16.03 O., according to Schwarz =  $C^{18}H^{15}O^3$  (perhaps dumasine ix. 25? Kr.); that which volatilises at  $100^\circ$  contains 77.61 p. c. C., 11.29 H., and 10.10 O., according to Schwarz =  $C^{28}H^{25}O^3$  (phorone xiii, 342? Kr.), and that which volatilises at  $150^\circ$  contains 74.40 p. c. C., 10.15 H., and 15.45 O., according to Schwarz =  $C^{20}H^{17}O^3$ .—The mixture of these compounds, treated with oxidising agents, yields fatty acids and a neutral oil containing 76.60 p. c. C., 10.48 H., and 12.92 O. The same mixture, boiled for some time with potash-ley, becomes dark-coloured and yields resin and a mobile oil containing 72.01 to 73.46 p. c. C., and 10.61 to 10.08 H. The latter is further decomposed by hot nitric acid, yielding oxalic acid and a new volatile oil (78.68 p. c. C., 10.59 H., and 10.63 O. =  $C^{10}H^8O$ : Schwarz). It is also decomposed by oil of vitriol or anhydrous phosphoric acid, producing a hydro-carbon (89.81 p. c. C. and 10.18 H. =  $C^{12}H^8$ , Schwarz), whose boiling point lies at about  $180^\circ$ , differing, therefore, from that of cumene and that of mesitylene (R. Schwarz, *Wien. Akad. Ber.* 5, 159; *J. pr. Chem.* 51, 374).

25. Cane-sugar solution heated with *basic nitrate of bismuth*, does not alter it, or merely gives it a faint yellowish colour. (Böttger, *Jahrb. pr. Pharm.* 22, 23.)—26. Boiled with *acetate of zinc*, it gives off a trace of carbonic acid. (Peschier, *J. Pharm.* 3, 508.)—27. A clear mixture of cane-sugar and aqueous *protochloride of tin*, kept in a sealed tube, deposits a white precipitate, without further alteration. In contact with the air, it turns brown after some hours, and gives off an odour of caramel. (Béchamp, *N. Ann. Chim. Phys.* 54, 38.)

28. When an aqueous solution of 1 pt. cane-sugar and 15 to 30 pts. 5-hydrated *bichloride of tin* is evaporated to dryness, and the residue heated to  $120^\circ$ — $130^\circ$ , it blackens and is converted into Maumené's caramelin  $C^{12}H^4O^4$ . This black-brown caramelin, insoluble in water, dilute acids, and alkalis is (different from Gélis's caramelin, and) formed from sugar by abstraction of 7 at. water:  $C^{12}H^{11}O^{11} = C^{12}H^4O^4 + 7H_2O$ . (Maumené, *Compt. rend.* 30, 314, 447; 39, 422.) With a smaller quantity of chloride of tin (*protochloride of mercury* or *terchloride of antimony*), a brown substance partially soluble in water is produced, perhaps a mixture of caramelin and unaltered sugar.—This re-action is applied by Maumené to the detection and estimation of sugar; but all carbohydrates behave in the same way.

29. When the compound of cane-sugar with *oxide of lead* is heated for three hours to  $168^\circ$ , the residue decomposed under water by hydro-sulphuric or carbonic acid, yields a colourless solution, from which by evaporation a transparent non-solidifying syrup is obtained. (Berzelius, *Jahresber.* 19, 442.) See below. When neutral acetate of lead is boiled for some time with solution of cane-sugar, a brown precipitate is obtained. (Peschier, *J. Pharm.* 3, 508.)

30. *Sesquichloride of iron* is reduced to protochloride by heating

with cane-sugar solution, without evolution of carbonic acid. Cane-sugar heated with ferric oxide, sulphuric acid, and water, yields formic and carbonic acids. (Hünefeld, *J. pr. Chem.* 7, 44.)—With *ferric acetate*, cane-sugar solution gives off a small quantity of carbonic acid, and deposits ferrous oxide. (Peschier, *J. Pharm.* 3, 508.)—When 1 pt. of *iodide of iron*, 1 pt. cane-sugar, and 4 pts. water are evaporated together to dryness, the residue, after standing for a week, gives up a portion of its substance to water. The dark-brown filtrate contains iodide of iron, but is no longer capable of fermenting with yeast. The residue is a black-brown powder which is slowly decomposed by hydrochloric acid into a brown solution and cinnamon-brown flocks, gives off iodine when heated, and leaves charcoal, after the combustion of which ferric oxide remains. Soda-ley withdraws iodine from the residue and leaves a mixture of ferric oxide and charcoal. (Frickhinger, *Repert.* 85, 210.)

31. When a strong solution of cane-sugar is boiled with a few lumps of potash, then diluted with water, and *nitrate of cobalt* added, a beautiful violet precipitate is formed which turns greenish on standing. The presence of grape-sugar prevents the formation of the precipitate. (Reich, *J. pr. Chem.* 43, 72.)

32. With *Cupric Salts*.—Cane-sugar solution left in contact with *cupric hydrate* for a week in the cold, neither alters its colour nor gives off carbonic acid; but after from 4 to 6 hours' boiling—the water which evaporates being replaced—cuprous oxide begins to form. (Busch, *Ann. Pharm.* 4, 60.) Cupric hydrate preserves its colour when left to stand in the cold, or when boiled for a short time with syrup of cane-sugar, but after longer boiling it gives up its water, turns brown, and after two hours' boiling is reduced to yellow cuprous oxide. If the syrup contains a trace of alkali, the cupric hydrate dissolves immediately, and is then precipitated by the sugar as cuprous oxide, this solution and precipitation going on till the whole of the cupric oxide is reduced. (Hunton, *Lond. Ed. Mag. J.*, 11, 154.) When cupric hydrate washed with cold water, is boiled with cane-sugar solution and a little caustic alkali, the colourless liquid filtered from the precipitated cuprous hydrate contains oxalic acid (J. J. Pohl, *J. pr. Chem.* 63, 359), carbonic and acetic acids. (Becquerel, *Ann. Chim. Phys.* 47, 5.) Ignited cupric oxide is not altered by boiling for several hours with solution of cane-sugar, but in presence of lime or alkalis, it dissolves and is precipitated as cuprous oxide. (Hunton.) When cupric hydrate is heated for a short time with cane-sugar, and a quantity of potash not sufficient for complete solution, a permanent green colour is produced. (Pohl.)—Cane-sugar boiled with aqueous *cupric sulphate* throws down metallic copper (from which aqueous ammonia removes a brown-red film), while a small quantity of cuprous salt remains dissolved. (Vogel, *Schw.* 13, 102.) The concentrated solution of equal parts of cupric sulphate and cane-sugar acquires by boiling, a blue-green, dark-green, and finally dark-brown colour, and deposits metallic copper, after the removal of which the supernatant liquid again appears green. On boiling the liquid for several hours and replacing that which evaporates, it becomes dark-brown, viscid, and smells like caramel. (Pohl.) The solution of equal parts of cupric sulphate and cane-sugar yields, on addition of soda-ley, a precipitate of cupric hydrate, which redissolves with deep-blue colour in excess of soda-ley, and is precipitated as red cuprous oxide when heated. (Mit-

schерlich, *Pogg.* 49, 402.) If a sufficient excess of alkali is present, the blue solution remains unaltered in the cold for several days, and deposits a small quantity of cuprous oxide only after some weeks. The reduction does not take place till after some time, even on boiling. (Trommer, *Ann. Pharm.* 39, 360.) After 14 days' standing in closed vessels, it deposits a green-blue precipitate and cuprous oxide. (Schwertfeger, *Jahrb. pr. Pharm.* 7, 292.) — When cane-sugar is boiled with *cupric chloride*, the liquid on cooling deposits cuprous chloride; from *cupric nitrate* nothing is precipitated on boiling, but the liquid afterwards yields a yellow precipitate with potash. From *cupric acetate*, cane-sugar precipitates on boiling (slowly in the cold, more quickly at  $36^{\circ}$ : Postel, *J. Pharm.* 18, 570), a large quantity of cuprous oxide containing organic matter, whilst a deliquescent sugar remains in the liquid. (Vogel; Buchner, *Schw.* 14, 224.) At the beginning of the boiling, a small quantity of carbonic acid is evolved. (Peschier, *J. Pharm.* 3, 508.) After half-an-hour's boiling of 1 pt. verdigris, 48 pts. water, and 48 pts. sugar, the whole of the copper is precipitated as cuprous oxide, together with a colourless jelly soluble in water. (Holger, *Zeitschr. phys.-math.* 3, 401.) According to Baumann (*N. Br. Arch.* 37, 47), cane-sugar solution is not altered by boiling with cupric sulphate, chloride or acetate, or with cuprammonia.

33. *Mercuric oxide* boiled with an aqueous solution of cane-sugar is converted into a black powder containing mercurous oxide. (Vogel). From solution of *mercuric chloride*, cane-sugar at the boiling heat, throws down calomel (Vogel), a dirty brown precipitate (Peschier); from *mercurous nitrate* it reduces the metal, together with a small quantity of mercurous oxide, and converts *mercuric acetate* into mercurous acetate. (Vogel, *Schw.* 13, 162; Buchner, *Schw.* 14, 224.) According to Baumann, mercurous nitrate is not reduced by sugar at the boiling heat.

34. Cane-sugar triturated with *nitrate of silver* soon becomes moist, and reddens the more quickly as it is exposed to a brighter light. Aqueous cane-sugar mixed with nitrate of silver deposits (at the boiling heat, according to Vogel) a black powder (Rouchas, *J. Pharm.* 17, 116; *N. Tr.* 24, 2, 187) which appears to be a mixture of oxide and metal. (A. Vogel.) According to Baumann, aqueous nitrate or ammonio-nitrate of silver is scarcely reduced by boiling with cane-sugar solution. — *Chloride of silver* covered with concentrated potash-ley is reduced to the metallic state by cane-sugar. (Casaseca, *Compt. rend.* 32, 686; *J. pr. Chem.* 53, 318.)

35. Cane-sugar boiled with aqueous *bichloride of platinum* precipitates nothing, according to Baumann; a black-brown substance, according to Peschier. — 36. From aqueous *terchloride of gold* it precipitates first a light red, then a dark red powder. (Vogel, Buchner.)

37. When a mixture of cane-sugar, *bromide of ethyl*, and lumps of potash-hydrate is heated to  $100^{\circ}$  for several days, Berthelot's *ethyl-glucose* is obtained. (Berthelot, *N. Ann. Chim. Phys.* 60, 103; *Chim. organ.* 2, 301.)

38. A solution of *indigo* mixed with carbonate of soda is not decolorised by prolonged boiling with cane-sugar solution. (Mulder, *N. Br. Arch.* 105, 268.)

39. Cane-sugar is not altered either by *diastase* (Guérin-Varry, *Ann. Chim. Phys.* 60, 32), or by *emulsin*. (O. Schmidt.)

40. Moderately concentrated aqueous solutions of cane-sugar left in contact with certain nitrogenous bodies, at temperatures between 10° and 30°, undergo transformations distinguished by the names *Vinous*, *Lactous*, and *Mucous Fermentation*. (See vii, 96.)

A. *Vinous Fermentation*.—The clear juice of sacchariferous plants left to itself in contact with the air at temperatures between 20° and 24°, becomes turbid after a few hours, gives off carbonic acid, becomes warmer than the surrounding air, and remains in a state of transformation for an interval varying from 48 hours to several weeks, according to the temperature, the amount of sugar present, and the nature of the nitrogenous matters,—till in fact the whole of the sugar is decomposed. As soon as the evolution of carbonic acid is terminated, a substance previously suspended in it, the *ferment*, separates, partly carried upwards by adhering gas-bubbles, partly downwards, leaving the liquid clear, which then, in place of the sugar, contains alcohol, glycerin, and succinic acid. The ferment formed in this process, if introduced at about the same temperature, into a moderately dilute solution of pure sugar, induces therein also the decomposition of the sugar into the same products.

Solutions of sugar containing gluten altered by the process of germination or of mashing, undergo, on standing, an irregular fermentation, which however may be rendered regular by the introduction of a small quantity of ferment. Such is the case in the fermentation of beer-worts. — Comp. Ure (*J. pr. Chem.* 19, 183).—When albuminoidal substances, gluten, casein, or substances of like nature, are introduced into sugar solutions, and the liquids are exposed for some time to the air, sometimes vinous fermentation takes place, sometimes another kind of decomposition. See the details below.

The views of Schwann already mentioned (vii, 109) on the conditions of fermentation, and those of Cagniard de Latour on the nature of yeast, have been further developed by Mitscherlich, Blondeau, Schröder & Dusch, Van den Broek, Pasteur, and others, and may now be regarded as established. For the opposite views of Liebig, see *Handwörterb.* 3, 117; *Agricultur-chemie*, 5 Aufl. 469; this *Handbook*, vii, 109; of Schmidt, *Ann. Pharm.* 61, 168; of Schubert, *Pogg.* 147 and 397; of Döpping & Struve, *J. pr. Chem.* 41, 255; of Traube, *Pogg.* 103, 381; of Berthelot, *Compt. rend.* 50, 680; &c. &c.

α. Vinous fermentation is always produced under the influence of the vital energy of *yeast-cells* (*Bierhefe*, *Ferment alcoolique*, *Torvula cerevisiæ*: Blondeau de Carolles), either when beer-yeast is introduced into saccharine liquids in which it can grow, or when the liquid is of such a nature that yeast-cells can form in it spontaneously.

Vinous fermentation is produced by one particular fungus, lactous fermentation by another. (Blondeau, Pasteur.) The spores of yeast are universally diffused through the air, and produce yeast-cells whenever they come into a sugar-solution adapted to their development; air deprived of these bodies never excites fermentation.

Fermentation is in all cases preceded by the development of vegetable germs in the fermentable liquid. These germs are of various species, some of which develop themselves while others remain inactive, according as the liquid is or is not adapted to their development and sustenance. (Blondeau.)

A sugar-solution mixed with yeast ferments immediately; but the

juice of grapes and other fruits requires access of air to bring it into the fermenting state. If the air is excluded, expressed grape-juice does not ferment, but if oxygen has access to it, fermentation is set up. Grape-juice preserved for a year by Appert's method (vii, 100) ferments a few days after transference into another vessel. The same grape-juice passed up over mercury, without coming in contact with the air, does not ferment till oxygen gas is passed up to it. Hence, Gay-Lussac regarded oxygen as essential to the commencement of fermentation in fruit-juices, but not to its continuance. (Gay-Lussac, *Ann. Chim.* 76, 247.)

Air previously heated to redness cannot induce fermentation in a solution of sugar mixed with yeast and boiled, inasmuch as either unboiled organic matter or unignited air is necessary to the commencement of the process. (Schwann, *Pogg.* 41, 187; Ure, *J. pr. Chem.* 19, 187.) Wine-must boiled and enclosed in a bladder does not ferment even if suspended in fermenting must. It appears indeed that the access of a solid body from the air is essential to vinous fermentation, so that oxygen gas evolved from water by electrolysis is incapable of bringing boiled grape-juice into the fermenting state. (Helmholtz, *J. pr. Chem.* 31, 434.) The ferment of the air may likewise be retained by filtration through cotton; consequently sweet malt-wort in contact with filtered air does not ferment even for weeks. (Schröder & Dusch, *Ann. Pharm.* 89, 332.)

Fresh grape-juice which has never come in contact with atmospheric air, suffers no alteration for years when kept over mercury at a temperature between  $26^{\circ}$  and  $28^{\circ}$ . If oxygen gas previously heated to redness or filtered through cotton be brought in contact with it, the juice after some hours becomes darker, absorbs the oxygen, and gives off carbonic acid, but no fermentation takes place even after a long time. Common air, inasmuch as it contains bodies capable of forming yeast-cells, or the yeast-cells themselves (even such as have never been in contact with the air) can set up vinous fermentation, the continuation of which is promoted entirely by the growth of the yeast-cells. (Van den Broek, *Ann. Pharm.* 115, 75.)

The fungi diffused over the surface of fruits, leaves, and fruit-stalks, likewise induce fermentation in saccharine liquids. If to a fermentable fruit-juice mixed with sugar, there be added 2 measures of water, the whole violently and continuously shaken, and the liquid, which has become specifically lighter, set aside, the cells of the fungi rise to the surface, and then give rise to formation of mould, but no fermentation takes place within the liquid. (H. Hoffmann, *Ann. Pharm.* 115, 228.)

If the motes floating in the air are collected in cotton or asbestos contained in a tube through which the air is drawn, and introduced into sugar-solutions which have been well boiled and cooled again, and are mixed with the mineral and albuminoidal constituents of yeast, they develop into *infusoria* and *mucedineæ*, even if only ignited air has access to the liquid. Sugar-solutions mixed with the same yeast-constituents, but not containing this dust, undergo no alteration between  $28^{\circ}$  and  $30^{\circ}$ ; neither do those into which cotton or asbestos alone is introduced. The same liquid remains unaltered if boiled in a glass flask, the neck of which is bent so that no dust can fall into it, the flask being afterwards left unclosed. (Pasteur, *Compt. rend.* 50, 303. see also *N. Ann. Chim. Phys.* 64, 5.)

The better a saccharine liquid is adapted for the nutrition of yeast-cells, the more easily will they be developed (from the above-mentioned bodies in the atmosphere) when air has access to the liquid. Thus vinous fermentation is almost always set up when the clear-filtered wash-water, or the decoction, of yeast (which contains the soluble mineral and albuminoidal constituents of that substance) is mixed with sugar-solution and left to itself (as observed long ago by Colin); it is frequently also accompanied by lactous fermentation; but the latter very seldom takes place alone, unless the wash-water of previously altered yeast has been used (Pasteur). All natural saccharine juices which ferment spontaneously yield a deposit of yeast (Thénard, Mitscherlich). Also diabetic sugar (Quevenne, *J. Pharm.* 24, 36). Yeast is formed in liquids containing putrefying animal matters, on addition of sugar, the formation of vibrios continuing if the sugar is present in small quantity only, but being hindered by a larger quantity (Mitscherlich, *N. J. Pharm.* 4, 218). A similar observation was made by Cagniard de Latour. Hence there can be no doubt that, in the following cases also, the occurrence of vinous fermentation depends upon the previous formation of yeast. Vinous fermentation is produced in sugar-solutions, after access of air, by the glutinous matter suspended in currant-juice, but not by the soluble part alone (Thénard), by white of egg (Seguin), gliadin (Taddei), legumin, especially if in a state of incipient putrefaction (Braconnot), by wheat-glutin, vine- and sorrel-leaves, mashed elder-flowers (Fabroni), ox-blood, the fibrin and serum of blood (Colin), comminuted brain (Pouchet, *Compt. rend.* 52, 284), and many other bodies. Honey dissolved in 4 pts. of water ferments without addition of yeast (Colin). Fermenting liquids exposed to the air after boiling, gradually pass into the fermenting state again (Gay-Lussac). Sugar-solutions cannot be brought into the fermenting state by wood-charcoal, the charcoal obtained by igniting animal matters with potash and lixiviating the residue, or platinum-black (Berzelius).

The vinous fermentation of sugar is likewise induced by the peculiar ferment of madder (Schunck's *erythrozym*) in contact with air, especially if this substance is in a state of decomposition. A mixture of carbonic acid and hydrogen is evolved; and the liquid, after 14 days, contains alcohol, acetic acid (perhaps, also, formic acid), a small quantity of succinic acid, and a sweet, brown, uncrystallisable body (glycerin? Kr.), but no lactic acid. The same effect is likewise produced by the brown precipitate formed on adding a small quantity of hydrochloric acid to an aqueous infusion of madder after it has been made alkaline by lime-water (Schunck, *J. pr. Chem.* 63, 222).

The clear filtrate of almonds bruised with water quickly brings grape-sugar into full fermentation, without at first producing yeast-cells perceptible by the microscope, these cells making their appearance only at a later stage of the process. The sacchariferous(?) liquid, if left to itself after the fermentation is ended, becomes filled with aggregates of cells, but putrefaction does not take place within 8 to 14 days. The fungi thus formed, if introduced into a fresh solution of grape-sugar, continue to grow in it, but produce only a slight and very transient fermentation, or none at all. When muscle, gelatin, or yeast, in a state of stinking putrefaction, is introduced into a solution of sugar, the putrefaction ceases, fermentation is set up, and yeast-cells are produced. (O. Schmidt, *Ann. Pharm.* 61, 168;



*Lieb. Kopp. Jahresber.* 1847-48, 468.) Hence Schmidt (like Liebig) regards the growth of fungi in fermentation as merely a secondary phenomenon, not an essential condition of the fermentation. But R. Wagner (*J. pr. Chem.* 45, 241) observed the simultaneous occurrence of fermentation and formation of yeast-cells under the conditions described by Schmidt.

Yeast consists of very small microscopic, round, or egg-shaped balls (Leuwenhoeck, Cagniard de Latour) of  $\frac{1}{1000}$  mm. diameter (Blondeau). These balls are vegetable cells (Cagniard de Latour), with elastic walls, filled with a liquid and a soft horny mass, which latter is at first attached to the walls, but extends to the middle as the cell grows; young cells are transparent, and almost destitute of granular contents. (Mitscherlich, Pasteur.) These cells multiply by gemmation (Cagniard de Latour, Mitscherlich); the newly formed cells do not separate from the central cell till they have attained to nearly the same size. (Pasteur.) They always remain isolated, and never form ramifications or elongated cells, like those of lactous ferment. (Blondeau.)

According to Cagniard de Latour, Turpin, and Mitscherlich, yeast-cells also increase by bursting and diffusing their granular contents through the liquid, the granules then developing into cells. Schlossberger and Pasteur did not observe this mode of formation, which is likewise inconsistent with the uniform size of the free yeast-cells. — Yeast contains cellulose, fat, nitrogenous and mineral substances. See analyses of yeast by Payen (*Mém. des Savants étrangers*, 9, 32); Dumas (*Traité de Chimie*, Paris, 1843, 6, 316); Mitscherlich (*Lehrb.* 4 Aufl. 370); Schlossberger (*Ann. Pharm.* 51, 193).

The yeast deposited in the vinous fermentation of beer, of diabetic urine, of grape-juice or other natural fruit-juices, is invariably of the same composition. (Quevenne, *J. Pharm.* 24, 265.) — In commercial beer-yeast, the cells of *Torula cerevisia* and of *Penicillium glaucum* may be distinguished by the aid of the microscope. These two fungi may be separated one from the other, by washing and filtration, the larger cells of the *Torula* remaining on the filter (and exciting vinous fermentation when introduced into sugar-solutions), while the smaller cells of the *Penicillium* pass through the filter and, consequently, the filtrate excites lactic acid fermentation in sugar-solutions. (Blondeau.)

On the distinction between top- and bottom-yeast, see Mitscherlich (*Pogg.* 59, 94); R. Wagner (*J. pr. Chem.* 45, 241); on beer-yeast in general, Colin (*Ann. Chim. Phys.* 30, 42).

Fermentation takes place only when the solution is sufficiently diluted with water; with less than 4 pts. water to 1 pt. sugar, it takes place but imperfectly or not at all, partly perhaps because the resulting alcohol precipitates the nitrogenous substances, destroys the fermentative power of the yeast, or renders the liquid unfit for its further development. If, on the other hand, the liquid is too dilute, the fermentation is slow, irregular, and easily passes into acetous fermentation. Moreover it is necessary that the yeast be in direct contact with the sugar-solutions. A solution of sugar contained in a bladder suspended within a fermenting liquid, does not ferment, but merely takes up a little alcohol by diffusion. (Helmholtz, p. 266.)

When a tube, plugged with filtering paper and containing yeast, is introduced into a sugar-solution, this solution passes through the paper and ferments within the tube, but not outside. (Mitscherlich,

*N. Ann. Chim. Phys.* 7, 30.) When a solution of sugar contained in a test-tube is separated into two parts by a cotton plug, and yeast is introduced into the upper part, this part ferments, but not the lower. (H. Hoffmann, *Ann. Pharm.* 115, 228.)

An increase of yeast takes place in fermentation, when the liquid, in addition to sugar, contains a nitrogenous substance. When, on the contrary, yeast is left in contact with a pure solution of sugar, it diminishes both in weight and in fermenting power, and in the end becomes totally inactive. (Payen, Quevenne.)

In the fermentation of pure sugar-solutions, the yeast first increases in weight and then diminishes, because it first assimilates the constituents of sugar, and gives them up again as the fermentation progresses. (Quevenne, *J. Pharm.* 27, 593.)

Yeast may grow and increase in sugar-solutions if they are mixed with ammoniacal salts, yeast-ash, and a trace of yeast,—fermentation then also ensuing.

If to 10 grs. of sugar-candy there be added 1 gr. of yeast-ash, 0.1 gr. tartrate of ammonia and a piece of moist yeast of the size of a pin's head, carbonic acid begins to escape after the lapse of 24 to 36 hours, and in the following days yeast separates out. In the latter, the microscope will distinguish the old cells added to the liquid from the transparent younger cells. In time however these differences disappear, and the whole of the yeast assumes the granular aspect of old washed yeast. If the constituents of the ash or the ammonia-salts are absent no fermentation takes place; if the yeast cells are absent, infusoria and lactous ferment are produced, but no yeast cells, apparently because the liquid is not adapted for their development (from the spores contained in the air). If the mixture be boiled, and afterwards brought in contact only with heated air, no fermentation of any kind takes place.

Sugar-solution mixed with white of hen's egg, passes, in the course of 3 or 4 weeks, into a state of slow fermentation and deposits cells of yeast (Colin & Thénard, Turpin). Even when yeast-cells are added, this fermentation does not take place till the albumin has passed into a state of decomposition. But blood-serum, flesh-juice, and the wash-water of yeast may serve for the formation of yeast without further aid, so that, after addition of sugar, yeast-cells are actively developed in these liquids (Pasteur).

Yeast grows and multiplies in pure sugar-solutions as well as in such as have been mixed with albuminoid substances. In the former case all the yeast-cells are found, at the end of the fermentation, to be deprived of their soluble nitrogenous constituents, which have been used for the formation of new yeast-cells; in the second case, there are found, together with the exhausted cells, a large number of newly-formed cells filled with soluble mineral and albuminoid substances (Pasteur).—When sugar-solutions are fermented with 15 to 20 per cent. of moist yeast, the quantity of yeast found at the end of the fermentation is less than that originally contained in the liquid. If, on the contrary, the weight of the yeast was 10 p. c. or less of that of the sugar, it increases during the fermentation. But if to the weight of the recovered yeast, there be added that of the nitrogenous substances which have passed into the solution, the sum of the weights of the two substances exceeds that of the yeast originally employed by 1.2 to 1.5 p. c. of the sugar. If albuminoid substances are like-

wise added, they are consumed in the formation of yeast; so that here also the weight of the yeast separated at the end of the fermentation, together with that of the yeast-constituents which have passed into the solution, is somewhat greater than the weight of the albuminoidal substances used (Pasteur).

When yeast mixed with sugar-solution and albuminoidal substances is exposed to the air in shallow vessels, oxygen is absorbed, and a quick and active increase of the yeast-cells takes place, only 6 to 8 pts. of sugar being decomposed for every 1 pt. of the newly-formed yeast. The yeast thus formed, if introduced into sugar-water without coming in contact with the air, immediately excites very active fermentation. (Pasteur, *Compt. rend.* 52, 1260). Hence Pasteur concludes that yeast can live in two different ways, either without contact of air, in which case it decomposes about 100 times its weight of sugar, growing and multiplying but slowly, or in contact with the air, in which case its reproduction goes on very quickly, but only a small quantity of sugar, or, under favourable circumstances, perhaps none at all, is converted into alcohol and carbonic acid.—With free access of air, yeast may grow in solutions containing albuminoidal substances, but no sugar whatever, or only milk-sugar (Pasteur, *Bull. Soc. Chim. Paris*, 1861, 79).

Thénard (*Ann. Chim.* 46, 294) fermented 100 pts. of sugar with 20 pts. of beer-yeast, and obtained 13·7 pts. of insoluble residue, which, when brought in contact with a larger quantity of sugar, diminished to 10 pts. The latter was white, resembled woody fibre, and was no longer capable of exciting fermentation.

The quantity of yeast must bear a definite proportion to that of the sugar; if the sugar is in excess, part of it remains undecomposed or merely undergoes a very slow after-fermentation, often going on for years.—If, after all the sugar is decomposed, the fermented liquid remains in contact with the yeast, or with nitrogenous matter not wholly converted into yeast, putrefaction may ensue.

Sugar-solutions containing a sufficient quantity of yeast, ferment completely in two or three weeks, unless lactic acid fermentation takes place. But an extremely protracted fermentation ensues when yeast is mixed with excess of sugar. In this case, the yeast lives at the expense of the soluble nitrogenous substances, and after these are used up, the younger cells continue to grow at the expense of the older (Pasteur).

During fermentation, part of the yeast is resolved into soluble products (Thénard).—The yeast recovered from pure sugar-solutions after fermentation is less rich in nitrogen than the original yeast, partly because its weight has been increased by the addition of non-azotised matter from the sugar, partly because a portion of its own nitrogenous substance has passed into the solution. On the other hand, it contains more woody fibre and fat than before fermentation; these substances have therefore been formed from the sugar. The yeast formed in sugar-solutions mixed with ammonia-salts, yeast-ash, and traces of yeast-cells, contains fat (Pasteur). Thénard (*Ann. Chim.* 46, 294) supposed that yeast might be obtained free from nitrogen by fermentation with excess of sugar.

The nitrogen of yeast is not converted into ammonia during fermentation; on the contrary, any ammonia that may be added disappears wholly or partially (Pasteur). Döbereiner supposed that the nitrogen of yeast was converted into ammonia during fermentation.

When sugar is fermented with the water obtained by washing beer-yeast (which has dissolved out the soluble constituents of the yeast), and with a trace of yeast-globules, scarcely half the original quantity of ammonia is found in the yeast at the end of the fermentation. In other cases, scarcely any ammonia is found in the liquid after fermentation. When tartrate of ammonia was added to the solution before fermentation, the fermented liquid contained free tartaric acid, and only  $\frac{4}{5}$  of the ammonia added (Pasteur).

When sugar-solutions are fermented with a very large excess of yeast, the formation of alcohol and carbonic acid goes on, even after all the sugar is decomposed, at the expense of the non-azotised matter of the yeast, so that the amount of these two products obtained is more than equivalent to that of the sugar.

The production of additional quantities of alcohol and carbonic acid at the expense of the substance of the yeast does not take place invariably when the small quantities of yeast absolutely required for the fermentation are exceeded, not even when 40 pts. of moist yeast (corresponding to 8 pts. of the dry substance) are added for every 100 pts. of sugar, but only when the yeast is in very large excess. Sugar yields, with an equal weight of moist yeast, scarcely more carbonic acid than corresponds to its weight; with 5 to 7 pts. moist yeast, from  $\frac{1}{30}$  to  $\frac{1}{20}$  more, but with  $23\frac{1}{2}$  pts. dry yeast = (110 pts. moist), it yields about three times as much. The weight of the additional quantity of alcohol produced is likewise equivalent to that of the carbonic acid.—Very active yeast, kept under water, undergoes a similar fermentation at the expense of its own substance, before it passes, by long keeping, into the putrefactive state (Pasteur).

Yeast loses a considerable portion of its fermenting power by pressure, and still more by washing with water (p. 267).—After thorough drying, its power of exciting fermentation is for the most part destroyed. This statement is opposed to that of Cagniard de Latour.—It likewise becomes inactive when heated either alone or with water. Dried yeast excites fermentation even after cooling by solid carbonic acid. (Cagniard de Latour).—Yeast crushed on the grindstone no longer excites fermentation (Lüdersdorff, *Pogg.* 67, 409), or only after a considerable time (Wagner); it then excites lactous fermentation. (C. Schmidt.) Yeast altered by too long-continued putrefaction, is inactive; but if the putrefaction has been less prolonged, it may be checked and converted into fermentation by addition of sugar. (Schlossberger, *Ann. Pharm.* 51, 211).—The fermentative power of yeast is destroyed by all substances which exert a poisonous action on fungi, but not by such as kill animals. (Schwann; Mitscherlich, *N. J. Pharm.* 4, 218.) Yeast sprinkled with alcohol, loses its fermentative power, which is not transferred to the alcohol.

The action of yeast on sugar is prevented by too great concentration of the solution, whether due to alkaline chlorides, gelatin, glycerin, or sugar. (Berthelot, *N. Ann. Chim. Phys.* 50, 352.) Strong mineral acids, added even in small quantity, prevent the fermentation, phosphoric acid alone acting favourably. (Wagner, *J. pr. Chem.* 45, 241.) Sulphuric acid does not accelerate the fermentation of sugar (Rose); sulphurous acid stops it. (Henry, *Ann. Chim.* 76, 290; Gay-Lussac.) Water saturated with bisulphide of carbon does not prevent fermentation, at least not completely. (Berthelot.) Arsenious

acid does not prevent fermentation. (Quevenne, Schlossberger.) According to Rousseau, vegetable acids are essential to fermentation; according to Anthon, they are injurious. Small quantities of formic, oxalic, or acetic acid, destroy the activity of ferment (Döbereiner); acetic acid, and especially lactic acid, act favourably, according to Mulder and Wagner, unfavourably according to Dumas and Anthon (*Dingl.* 153, 303; 154, 223); tartar acts favourably with cane-sugar according to Rose, injuriously with fruit-juices or grape-sugar, according to Anthon. The juice of unripe gooseberries or currants mixed with grape-sugar ferments more completely when neutralised with carbonate of lime than in the sour state. (Anthon, *Dingl.* 153, 385). The fermentation of sugar-solutions mixed with yeast goes on most quickly when the liquid is kept neutral by addition of carbonate of lime, the action not being necessarily accompanied by formation of lactic acid. But such a liquid also promotes the development of lactic ferment, so that a portion of the sugar is apt to be converted into lactic acid. (Pasteur, *N. Ann. Chim. Phys.* 52, 415.)—Fermentation is not prevented by the oxides of zinc, lead, and copper, the carbonates of baryta, magnesia, manganese, and nickel, or even by metallic iron or ferrous carbonate; but soluble iron-salts partly prevent fermentation, and ferric sulphate added to the amount of 30 p. c. of the sugar, stops it entirely. A similar counteracting effect is produced by peroxide of manganese, carbonate of copper, carbonate of lead, and soluble lead-salts. (Berthelot.) Mercuric oxide destroys the fermentative power of yeast. (Colin.) Fermentation is retarded by potash or lime (Cruikshank), by soaps (Wagner), interrupted by a small quantity of common salt. (Döbereiner.) Fermentation is not prevented, or at least not completely, by bicarbonate of potash or carbonate of soda, to the amount of 10 p. c. of the sugar (50 p. c. stops it completely), sulphate of soda or sulphite of lime; it is not prevented by hyposulphite, borate or phosphate of soda, or by tartar emetic (Mitscherlich), extract of nux vomica (Schwann, Ure), quinine or strychnine (Wagner). Wine-must added to mustard-powder or oil of mustard does not ferment in 8 months. (Fontenelle, *J. Pharm.* 9, 437.) Oil of turpentine does not prevent the action of yeast upon sugar. (Berthelot.) Yeast-cells sown in onion-juice expressed and mixed with sugar, never develop themselves, unless the volatile oil is driven out by boiling. (Pasteur, *N. Ann. Chim. Phys.* 52, 416.) On the influence of various bodies on vinous fermentation, see also Leuchs *Chem. Centr.* 1861, 385).

*β.* Cane-sugar does not undergo vinous fermentation, till, under the influence of a peculiar substance in the yeast, or of a substance contained especially in the kernel of fruits, it has been resolved, with assumption of water, into lævo- and dextro-glucose. (Dubrunfaut, Berthelot, Buignet). In this re-action, the specific gravity of the cane-sugar solution increases (Graham, Hoffmann & Redwood, *Chem. Soc. Qu. J.* 231; *Lieb. Kopp. Jahresber.* 1852, 801).

Cane-sugar does not split up into alcohol and carbonic acid, till it has taken up an atom of water (Dumas & Boullay, *Ann. Chim. Phys.* 37, 46). It is converted, previous to fermentation, into uncrystallisable (Dubrunfaut, 1838), lævo-rotatory sugar (Persoz, *Compt. rend.* 17, 755; *N. Ann. Chim. Phys.* 18, 102), into grape-sugar (Rose, *Pogg.* 52, 293). The spontaneous fermentation which sacchariferous vegetable juices undergo on standing, produces inversion of the cane-sugar contained

in them. (Biot, *Compt. rend.* 15, 528; Hochstetter, *J. pr. Chem.* 29, 29.) The conversion of cane-sugar into uncrystallisable sugar is likewise produced by boiling with nitrogenous substances (Hochstetter).

Cane-sugar solution in contact with washed yeast does not ferment for a month at 20° or even at 38°, whereas grape-sugar ferments completely under similar circumstances. It is not till a six- or eight-fold quantity of yeast has been added, that slow fermentation takes place, the larger quantity of yeast first converting the cane-sugar into grape-sugar. If the fermenting cane-sugar solution is mixed with a quantity of alcohol sufficient to stop the fermentation, and the filtrate evaporated to a syrup, a non-crystallisable mass is obtained resembling honey, and behaving with potash like grape-sugar (Rose). Grape-sugar certainly ferments somewhat better and more quickly than cane-sugar, but without exhibiting the great differences mentioned by Rose. The same quantity of yeast suffices for both kinds of sugar. (Pasteur, *N. Ann. Chim. Phys.* 58, 357.) The sugar produced from cane-sugar by the action of a ferment, cannot be obtained in the crystalline state, and is different from grape-sugar, polarising less strongly than granular sugar (*Krümelsucker*). This transformation of cane-sugar is produced by a substance which is present in the yeast-spherules and may be extracted by water. Consequently cane-sugar ferments with washed yeast less quickly than with fresh yeast. Ordinary unwashed yeast brings cane-sugar into fermentation as quickly as grape-sugar (Mitscherlich, *Berl. Akad. Ber.* 1841, 300; *Pogg.* 55, 222; *Berz. Jahresber.* 22, 482). According to a former view, which Pasteur (*N. Ann. Chim. Phys.* 58, 357; *Compt. rend.* 50, 1083) still endeavours to maintain, the inversion of the cane-sugar is produced by the free acid of the fermenting liquid. This view is contradicted by the experiments of Mitscherlich, as well as by those mentioned on page 254, on the behaviour of cane-sugar with dilute acids at mean temperatures, and by the following. Succinic acid mixed with a cane-sugar solution to the amount of 0.38 p. c. does not produce inversion; but when yeast, which has been pressed, is suspended in 2 pts. of water, the liquid filtered, after some hours produces transformation of cane-sugar, even in an alkaline solution, but no fermentation or acidification. When the same liquid is mixed with its own volume of alcohol, white nitrogenous flocks are precipitated, which after being washed with alcohol and dried, become yellow and horny, and are capable of transforming from 50 to 100 pts. of cane-sugar. This substance may be continually reproduced from washed yeast by again leaving it in contact with water. (Berthelot, *Compt. rend.* 50, 980; *Rép. Chim. pure*, 2, 272.) When added to fruit-juices, it likewise transforms the cane-sugar into inverse sugar (Buignet, *N. Ann. Chim. Phys.* 61, 301). The nitrogenous matter of beet-juice also converts cane-sugar into uncrystallisable sugar; consequently solutions of raw sugar are more easily decomposed by boiling than solutions of refined sugar. At the same time, part of the nitrogenous matter becomes soluble and no longer precipitable by heat, lime, or tannic acid. (Hochstetter, *J. pr. Chem.* 20, 29.)

The cane-sugar in the expressed juice of the peach quickly undergoes this transformation on standing (even if the free acid has been neutralised); but if the juice is mixed with an equal quantity of alcohol and filtered from the resulting precipitate, the transformation is scarcely perceptible even after two months. The acid juice of

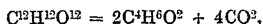
apricots may be kept for a while without much alteration; but if it be mixed with a small quantity of a solution obtained by extracting crushed gooseberries with water and filtering, a considerable portion of the cane-sugar in the apricot-juice undergoes transformation in 12 hours at ordinary temperatures. (Buignet.)

At the beginning of the fermentation, and even an hour afterwards, a solution of cane-sugar still exhibits dextro-rotatory power which, however, becomes lævo-rotatory after boiling with acids. Hence the transformation of the cane-sugar into inverse sugar takes place during the fermentation, not before, and is not quite complete even towards the end of the operation (Soubeiran, *N. J. Pharm.* 4, 347).

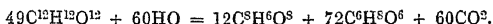
γ. When a solution of cane-sugar which has been transformed by acids, is fermented, the rotatory power of the fermenting liquid does not diminish till  $\frac{1}{2}$  or  $\frac{2}{3}$  of the sugar is converted into alcohol, but from this point a regular diminution of the lævo-rotatory power takes place, proportionate to the quantity of sugar decomposed. The cause of this alteration is, that during the first half of the fermentation 2 at. dextro-glucose disappear for every 1 at. lævo-rotatory fruit-sugar, whereas during the second half of the fermentation, 2 at. lævo-glucose are decomposed for every 1 at. dextro-rotatory grape-sugar. (Dubrunfaut, *N. Ann. Chim. Phys.* 21, 169; *Compt. rend.* 42, 904.) This behaviour of inverse sugar is designated by Dubrunfaut as *Fermentation alcoolique élective*.

So, according to Dubrunfaut. According to Soubeiran (*N. J. Pharm.* 4, 347) the solution of inverse sugar continues to exhibit lævo-rotatory power during the whole of the fermentation, this power, however, becoming weaker as the sugar is decomposed. More recently (*N. J. Pharm.* 16, 259), Soubeiran describes the following experiment: Cane-sugar completely inverted by oxalic acid and freed from that acid by addition of marble, exhibited when dissolved in water, 18° of lævo-rotation for 35.1 p. c. of inverse sugar in the solution. In the course of the fermentation, the lævo-rotation rose to 25°, at which point the solution contained 21.3 p. c. inverse sugar, then sank to 10°, when the sugar was reduced to 11.5 p. c. On Dubrunfaut's view, this and the following statements are unintelligible. (Kr.) The colourless inactive sugar obtained by heating cane-sugar with a little water to 160°, does not deflect the plane of polarisation at any time during its fermentation, but during the fermentation of fruit-sugar (inverse sugar is probably intended, inasmuch as Mitscherlich was not acquainted with pure lævo-rotatory fruit-sugar) the rotatory power of the liquid decreases in proportion as the sugar is decomposed, though it does not actually change from left to right. (Mitscherlich, *Berl. Akad. Ber.* 1843; *Pogg.* 59, 94; *N. J. Pharm.* 4, 216). When dextro-glucose is mixed with inverse sugar, these two kinds of sugar disappear during fermentation, simultaneously and in equal proportion, so that the cessation of the fermentation does not coincide with the disappearance of the inverse sugar. (Dubrunfaut). In fermenting honey, the lævo-rotatory power increases at first, in consequence of the inversion of the cane-sugar present; afterwards the fermentation proceeds like that of inverse sugar. But towards the end of the process, dextro-rotation appears again, so that the sugar, which disappears at last, appears to be a peculiar kind of dextro-rotatory sugar. (Dubrunfaut.)

δ. In vinous fermentation, the greater part of the sugar is resolved into alcohol and carbonic acid :



a smaller portion, not exceeding 4 or 5 per cent., being converted into glycerin, succinic acid, and carbonic acid. The yeast itself takes up a portion of the elements of the sugar, varying from 1 to  $1\frac{1}{2}$  per cent. of the whole, according to its quantity, in the form of cellulose and fat (Pasteur, *N. Ann. Chim. Phys.* 58, 330; Preliminary Notice, *Compt. rend.* 46, 179, and 857).—On the formation of cellulose from sugar during fermentation, see Terrell (*Bull. Soc. Chim. Paris*, 1861, 109), and Pasteur's remarks (*Ibid.* 111.) For the formation of succinic acid and glycerin, Pasteur gives the equation :



Lavoisier found the sum of the weights of the carbonic acid and alcohol nearly equal to the weight of the sugar employed. Gay-Lussac (*Ann. Chim.* 95, 318) calculated therefrom that 100 pts. cane-sugar should yield 51.34 pts. alcohol and 48.66 carbonic acid. Dumas & Boullay (*Ann. Chim. Phys.* 37, 45) showed that cane-sugar must take up an atom of water, before it can resolve itself into alcohol and carbonic acid. The acid present in vinous fermentation was regarded by Lavoisier and Thénard as acetic acid, by others as lactic acid. But the formation of lactic acid takes place only when its peculiar ferment is present, not during the fermentation excited by beer-yeast (Pasteur). The occurrence of *succinic* acid was formerly observed in the fermentation of honey, bread, and *Siliquea dulcis*, by Beissenhirtz (*Berl. Jahrb.* 1818, 158), of pea-flour with casein, by Dessaignes; in fermenting sugar-solution by Schmidt (*Lieb. Kopp. Jahresber.* 1847-8, 466); in the fermentation of sugar with madder-ferment by Schunck (*J. pr. Chem.* 63, 222). But Pasteur first showed that succinic acid is an essential and constant product of vinous fermentation, after Guérin-Varry (*Ann. Chim. Phys.* 60, 58) had pointed out that, in the fermentation of cane-sugar, 3.6 per cent. of the sugar is lost for the formation of alcohol and carbonic acid, because other products are likewise formed.

100 pts. of cane-sugar brought in contact with a quantity of yeast, which would have weighed 1.2 pts. in the dry state, yielded 0.673 pts. succinic acid, and 3.64 pts. glycerin. Part of the yeast was converted into soluble (acid) substances; but the weight of the yeast recovered from the fermented liquid was greater than that of the yeast originally employed, because it had assimilated the elements of the sugar. The soluble matter is a product of the decomposition of the yeast, and is formed in greater abundance in proportion as a larger quantity of yeast has been employed. The substance taken up by the yeast amounts to between 1 and  $1\frac{1}{2}$  per cent. of the sugar, if the fermentation is set up by adding to the sugar-solution albuminous substances and only so much yeast as is required for regular fermentation; it is contained in the yeast chiefly as fat and cellulose, and is produced in larger quantity when the sugar is in excess (Pasteur).

Glycerin and succinic acid are produced by the yeast itself, not by any peculiar ferment (such as the lactic acid ferment). Both these bodies, as well as the carbonic acid, are products of the decomposition of the



sugar, not of the yeast [it should perhaps be: their formation is a result of the vitality of the yeast, not of the decomposition of dying yeast (Kr.)]. They are always produced, whatever may be the temperature of the fermenting liquid, the atmospheric pressure, or the weight and variety of the sugar employed,—by old as well as by newly formed yeast, in acid as well as in neutral liquids, but more abundantly in the latter; in larger quantity also when the fermentation is comparatively slow. Their absolute quantity is variable; but their weights are for the most part in definite relation to one another (Pasteur).

When yeast is heated with solution of sugar to  $100^{\circ}$ , just after the fermentation has commenced, an abundant and continuous evolution of carbonic acid takes place, according to Quevenne (*J. Pharm.* 27, 603), and at the same time there is formed from the sugar, not alcohol, but a peculiar, uncrystallisable and non-fermentable substance. According to Berthelot, the carbonic acid evolved on heating is merely that which has been previously formed by the vinous fermentation, and the amount of sugar decomposed does not exceed that which corresponds to the carbonic acid. (*N. Ann. Chim. Phys.* 52, 362.)

Besides common alcohol, there are produced, during fermentation, small quantities of other alcohols especially *butylic alcohol* ( $C^4H^{10}O^2$ ), *amyllic alcohol* ( $C^{10}H^{22}O^2$ ), and others, but no methylic alcohol. On the formation of these bodies, see Maumené (*Compt. rend.* 45, 1021); Wurtz (*N. Ann. Chim. Phys.* 42, 129.)

The carbonic acid which escapes in fermentation is not mixed with any other gas. (Thénard).—Pasteur found  $\frac{1}{10,000}$  nitrogen, not proceeding from the yeast. So likewise Berthelot (*N. Ann. Chim. Phys.* 52, 362). It is quite free from hydrosulphuric acid. (Schlossberger, *Ann. Pharm.* 51, 203.) The bubbles of carbonic acid are never evolved from the yeast-cells, but always from particles of foreign bodies present in the liquid. (Pasteur.)

The gum, extractive matter and malic acid (Proust), the dextrin (Ventzke, *J. pr. Chem.* 25, 81) contained in fermenting liquids, are not altered by the fermentation.

*Lactous Fermentation.* See x, 76, and xi, 473. In the preparation of of lactic acid (xi, 475), the precipitate formed on the bottom and sides of the vessel from the chalk and the decomposition-products of the cheese is found, at the end of the fermentation, to be covered with a small quantity of a grey substance, the *lactous ferment*. When this substance is introduced into a cooled and clear-filtered decoction of beer-yeast, together with from 15 to 20 pts. of water, chalk, and a quantity of sugar equal to from  $\frac{1}{20}$  to  $\frac{1}{10}$  of the liquid, and this liquid is kept at a temperature of  $30^{\circ}$  to  $35^{\circ}$  for some days, a brisk evolution of carbonic acid and hydrogen takes place, the liquid becomes turbid and deposits a precipitate, and the chalk dissolves in the form of lactate of lime. The new (and already pure) lactous ferment separated at this stage of the process, if introduced, together with chalk, into sugar-water, produces within an hour, an incipient evolution of gas and conversion of the sugar into lactate of lime. (Pasteur, *N. Ann. Chim. Phys.* 52, 404.)

As yeast is necessary to vinous fermentation, so likewise does lactous fermentation require the presence of a peculiar substance, the *lactous ferment* (Blondeau, Pasteur). This ferment, according to Blondeau, is the *Penicillium glaucum*. When lactous fermentation is set up in suitable sugar-solutions merely left to themselves, it is because certain bodies present in the air develop, in the liquid, into cells of

lactous ferment, which then set up the fermentation. If, therefore, the air is excluded, or if only heated air has access to the liquid, no lactous fermentation will take place unless lactous ferment is added (Pasteur).

Lactous ferment, viewed in the mass, resembles beer-yeast; it is grey, slightly glutinous, and appears, under the microscope, to consist of very small spherules of  $\frac{1}{800}$  mm. diameter, some isolated, others united in groups, and possessing molecular motion (Pasteur). The cells of *Penicillium glaucum* have, at most, a diameter of  $\frac{1}{400}$  mm.; they increase at first, like the cells of yeast, by formation of new round cells, but afterwards by formation of elongated and many-branched cells, which ultimately cover the surface like a white mould (Blondeau).

A small quantity of lactous ferment is capable of decomposing a large quantity of sugar, provided the liquid is kept neutral by chalk, otherwise its action on the sugar is retarded by the free acid. It increases if nitrogenous matter, which may serve to nourish it, is likewise present. By desiccation or by boiling with water, its action is weakened, but not altogether prevented. It acts best on sugar when air is excluded, inasmuch as the action is then not interfered with, either by the formation of mould or by infusoria. If no other ferment is present, the lactous fermentation goes on regularly, and often more quickly than vinous fermentation (Pasteur).

In solutions of cane-sugar containing phosphoric acid and ammoniacal salts, *Penicillium glaucum* can grow and convert all the sugar into lactic acid (Pasteur, *Compt. rend.* 51, 298).

Previous to lactous fermentation, the liquid always becomes viscous, in consequence of the development of *Penicillium glaucum*, whose ramifications fill the liquid to such an extent that it does not run out when the vessel is inverted. If this plant can develop itself in sugar-solutions, lactous fermentation ensues whether the liquid is acid or alkaline. If the liquid also contains albuminous substances, these yield ammonia and carbonic acid for the development of the *Penicillium*, and are partially converted into butyric acid, while part of the sugar is transformed into mannite (Blondeau, *N. J. Pharm.* 12, 257).

The spontaneously developed fermentation of saccharine juices containing nitrogen, is sometimes lactous, sometimes vinous, most frequently both together.—If yeast (as is generally the case) contains the cells of *Penicillium glaucum*, as well as those of *Torula cerevisia*, vinous fermentation takes place first, then lactous fermentation, at the expense of still unaltered sugar. (Blondeau.) When sugar-solutions are brought into the state of lactous fermentation by cheese (or other nitrogenous substances) the lactic acid, formed after a while, prevents the further action of the ferment, but after repeated addition of bicarbonate of soda (Boutron & Fremy), or chalk (Pelouze & Gélis), the whole of the sugar is converted into lactic acid.—Slightly alkaline liquids are best adapted for the development of lactous ferment, neutral liquids for the development of yeast. (Pasteur.) The kind of fermentation, vinous or lactous, excited in sugar-solutions by a nitrogenous substance depends upon the stage of decomposition at which that substance has arrived. (Boutron & Fremy.)

Sugar-solutions undergo lactous fermentation in contact with various membranes, especially calf's rennet (Fremy, *Compt. rend.* 8, 96, and 9, 165; see also Gay-Lussac, *Compt. rend.* 9, 46), with diastase altered by exposure to the air—with the previously altered nitrogenous

substance of beet-juice — with decomposing animal bladder — with whey. (Boutron & Fremy, *N. Ann. Chim. Phys.* 2, 256; Blondeau.) — When urine, mixed with sugar, is left to itself, *Penicillium glaucum* becomes developed, and lactic acid is produced. (Blondeau.)

The soluble parts of gluten and casein, as well as the nitrogenous liquid which remains after vinous fermentation, are peculiarly well adapted for the development of lactous ferment; consequently, when these liquids are mixed with sugar and exposed to the air, ferment is formed in them, even if yeast is added, the two ferments then exerting their specific actions side by side (Pasteur); see also *Mucous Fermentation*, p. 280.

The solution of sugar in whey becomes so viscid in a few days, as not to run out when the vessel is inverted. Each drop of the liquid then exhibits under the microscope a large number of individual cells, and of intergrown shoots, which when developed rise to the surface and there fructify, so that the liquid becomes covered with a layer of mould. The mass which has then again become fluid, contains acetic, lactic, or butyric acid, according to the species of plant which has been developed in it. — If carbonate of ammonia has been added to the saccharine whey, no penicillium cells are formed in it, or only very few.

A mixture of 4 pts. sugar, 2 pts. chalk, 3 pts. cheese, and 20 pts. water exposed to a temperature between  $20^{\circ}$  and  $25^{\circ}$ , gives off, within the first 8 days, carbonic acid mixed with a very small quantity of hydrogen. In open vessels, the surface becomes covered with a layer of mould containing a large number of cells of *Penicillium glaucum*; the liquid becomes acid, viscous, and ropy, and the casein, in combination with the chalk, falls to the bottom. In the further progress of the fermentation, hydrogen is evolved as well as carbonic acid, the casein is converted into butyric acid, the sugar either into lactic and acetic acids, or into mannite. (Blondeau, *N. J. Pharm.* 12, 340.)

Also when the decoction of yeast, unmixed with cells of lactous ferment, is set aside with sugar and chalk, lactous fermentation sets in after contact with the air for a short time, generally, however, accompanied by another kind of fermentation (Pasteur). See *Mucous Fermentation*.

In liquids containing sugar, yeast-ash, and tartrate of ammonia (p. 269), infusoria and cells of lactous ferment are produced in contact with the air, even when small quantities of yeast are added. After a few days, the infusoria disappear, while the lactous ferment increases, and often remains as the only active ferment. When carbonate of lime is added to sugar-water containing small quantities of ammonia-salts and phosphates, and the liquid is exposed to the air, it begins, after 24 hours, to show turbidity and give off gas; the fermentation which ensues in the following days causes the ammonia to disappear, the carbonate of lime and the phosphates to dissolve, and produces lactate of lime and lactous ferment, which latter is usually mixed with infusoria (Pasteur, *Compt. rend.* 48, 337).

The fermentation observed by J. Gay-Lussac & Pelouze (*Ann. Chim. Phys.* 52, 411) in kept beet-juice, and by Fourcroy & Vauquelin in kept onion-juice, appears to have been partly lactous, partly mucous fermentation.

Sugar may be converted, by lactous fermentation, into lactic acid, without yielding other products of decomposition (Boutron).

Sugar in the state of lactous fermentation may be converted into

lactic acid, without yielding other products (Boutron & Fremy). The alcohol, gum, and mannite, which are sometimes produced in lactous fermentation, occur only when yeast or mucous ferment is mixed with the lactous ferment. (Pasteur.) The butyric acid is a product of the further decomposition of the lactic acid (x, 76). — Occasionally, sugar yields, under the influence of animal membranes, an acid different from lactic acid and forming a lime-salt soluble in alcohol. (Boutron & Fremy. See also Berthelot, *N. Ann. Chim. Phys.* 50, 359.) — Fremy assumed that the sugar was transformed, first into mannite, then into lactic acid.

When inverse sugar, formed from cane-sugar by the action of acids, is submitted to lactous fermentation, the lævo-rotatory power of the liquid is increased by  $\frac{1}{2}$  and then remains constant without further fermentation occurring. This increase of rotatory power, compared with the quantity of lactic acid that is formed, proves that only the dextro-glucose has been converted into lactic acid, while the lævo-glucose has remained unaltered (Dubrunfaut, *N. Ann. Chim. Phys.* 21, 175). Dubrunfaut himself does not consider his experiment conclusive; according to other statements, including those of Pasteur (*Compt. rend.* 51, 298), the whole of the sugar disappears in the lactous fermentation.

The lactous fermentation of sugar may be replaced, under apparently similar circumstances, by a conversion of the sugar into acetic acid. 500 grms. sugar dissolved in a litre of water, and set aside for a month, in contact with 300 grms. cheese, without access of air, and at a temperature of 20°, did not give off any gas, but formed a thick crust of mould and a large quantity of acetic acid. This transformation takes place under the influence of *Torrula aceti*. (Blondeau, *N. J. Pharm.* 12, 336.)

The molasses left in the manufacture of beet-sugar, if rich in nitrates, sometimes gives off nitrous acid during vinous fermentation, according to Pasteur (*Bull. Soc. Chim. Paris*, 11 Mar. 1859; *Kopp's Jahresber.* 1859, 553), only when it undergoes vinous and lactous fermentation at the same time. The nitrates are here reduced by the hydrogen evolved in the formation of lactic (more correctly, of butyric) acid.

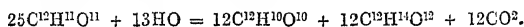
Aqueous sugar-solutions set aside for weeks or months at 40° or a lower temperature in contact with chalk and cheese (glue or other nitrogenous substances) undergo a fermentation different from the vinous, and not depending on the presence of yeast. In this fermentation, both the nitrogenous substance and the sugar are destroyed, carbonic acid, nitrogen and hydrogen escape, and alcohol, lactate of lime and butyrate of lime are produced (Berthelot, *N. Ann. Chim. Phys.* 50, 351).

Berthelot likewise designates this reaction as *Fermentation alcoolique*, whereas Pasteur (*N. Ann. Chim. Phys.* 58, 324) regards it as lactous fermentation. — 10 grms. cane-sugar, 120 grms. water, 10 grms. chalk, and 2 grms. cheese, yielded at 40° in six weeks, 1.2 grm alcohol, together with lactate of lime, ferment, and 3 grms. of unaltered sugar. — 170 grms. cane-sugar, 2 litres of water, 200 grms. chalk and 200 grms. cheese, at a temperature near 0°, yielded in five weeks, 10 grms. alcohol, together with lactate of lime and a small quantity of butyrate. In this reaction, neither mannite nor fat was formed. Yeast was not produced, if the process was conducted out of contact with air, or in an atmosphere of carbonic acid; nevertheless alcohol was obtained even under these circumstances. Compare the correspond-

ing experiments of Berthelot, under *Glucose*, *Mannite*, *Dulcite*, *Sorbite* and *Milk-sugar*.

*C. Mucous Fermentation.*—This is another kind of fermentation which cane-sugar undergoes, likewise under the influence of nitrogenous substances and in contact with air, but under circumstances otherwise not exactly known,—giving rise to the escape of carbonic acid and hydrogen, and the formation of mannite, a peculiar gum and a mucilaginous substance.

The mucous fermentation of sugar takes place (like vinous and lactous fermentation) under the influence of a peculiar mucous ferment. This ferment is composed of spherules from 0.0012 to 0.0014 mm. diameter, and when introduced into sugar-solutions containing albumin causes the sugar to be resolved into mannite, gum, and carbonic acid, 100 pts. cane-sugar yield, on the average, 51.09 pts. mannite and 45.5 pts. gum, corresponding to the equation :



When a larger proportion of gum is obtained, the liquid is observed to contain larger spherules, probably belonging to a peculiar mucous ferment (Pasteur, *Bull. Soc. Chim. Paris*. 1861, 30).

Mucous fermentation requires access of air and likewise the presence of nitrogenous matter; but the latter is capable of exciting mucous fermentation even after boiling. In this reaction, neither acid nor alcohol is produced. (Hochstetter.) Mucous fermentation is prevented by sulphuric acid, hydrochloric acid, or alum (Desfosses), by free mineral acids (Hochstetter, *J. pr. Chem.* 29, 30).

Syrup of cane-sugar which had been poured at the boiling heat into bottles in Martinique, the bottles being filled with it, underwent mucous fermentation on being transported to France and poured out into open vessels. (Peligot.)—Fresh beet-juice becomes gummy by contact with air, and then contains mannite, gum, lactic acid, and un-crystallisable sugar. These changes take place with greater facility when fermenting beet-juice is added to the fresh juice, even when the greater part of the nitrogenous matter has been removed by lime, and whether the quantity of free alkali present is great or small. Alcoholic fermentation sometimes sets in, if the acid is neutralised (Hochstetter).—When carrot-juice is left to itself between 30° and 40°, the cane-sugar which it contains is converted into glucose, mannite, lactic acid, and a gum isomeric with gum-arabic (Tilloy & MacLagan).

The expressed juice of mangold-wurzel begins to ferment in 3½ days, and the fermentation is complete in 2½ days. From the solution, clarified and evaporated to a syrup, alcohol of 80 p. c. precipitates a glutinous mucus, and the filtrate yields crystals of mannite. If the mucus be washed with alcohol, its aqueous solution precipitated with basic acetate of lead, the washed precipitate decomposed under water by hydrosulphuric acid, and the filtrate evaporated to dryness, a transparent, slightly coloured gum is obtained, containing 40.89 p. c. carbon, 6.10 hydrogen and 53.01 oxygen (Kircher, *Ann. Pharm.* 31, 337).

The juice of the sugar-cane contains a white non-azotised (?) substance, which becomes brown and moist in contact with the air, is soft and difficult to dry, soluble in water, insoluble in alcohol and ether, and is precipitated from its aqueous solution by oxide of lead, mercurous salts, and alcohol. It converts sugar into a substance intermediate

between starch and gluten, this substance being formed quickly and somewhat abundantly in syrups, and rendering them viscid, ductile, and uncrystallisable. If, therefore, the juice, after being treated with lime, is left to stand for 48 hours, a jelly is produced, from which alcohol throws down a soft, white, nacreous precipitate, which dries up to a nacreous mass, dissolves but sparingly in hot or cold water, even when moist, but swells up in it to a transparent mass, and when treated with nitric acid, yields nothing but oxalic acid. This mass is not coloured by iodine, or converted into sugar by dilute acids, and does not give off ammonia on dry distillation. It is found abundantly at the bottom of the vats in which molasses is left to ferment for the preparation of rum. (Plagne, *J. Pharm.* 26, 248.)

Lemonade containing sugar, volatile oil, citric acid, and condensed carbonic acid, loses its fluidity and becomes gummy by long keeping, especially in winter. If the gummy liquid be precipitated by alcohol, and the precipitate, which is friable when dry, be washed with alcohol, there remains, after drying at  $100^{\circ}$ , a viscid, semi-transparent, horny mass, while the alcohol takes up a brown, uncrystallisable sugar. This mass recovers its former appearance, when cold water is poured upon it, and forms with boiling water, a gum which is difficult to filter, is not coloured by iodine, does not reduce potassio-cupric tartrate or precipitate basic acetate of lead, and yields oxalic acid with nitric acid. This gum contains 1.37 p. c. ash, and after deduction of this ash, it contains, on the average, 43.56 p. c. C., 6.47 H., and 49.97 O., the lead-compound contains 55.80 p. c.  $\text{PbO.}$ , 19.31 C., 2.70 H., and 22.10 O. (Tilloy & MacLagan.)

When yeast is well washed with cold water, then boiled with water, and  $\frac{1}{5}$  pt. sugar dissolved in the filtrate, the liquid, after a few days, becomes turbid and tenacious, like decoction of linseed. At the same time, a mixture of carbonic acid and carbonic oxide in varying proportions is evolved. This fermentation lasts about 12 days, for a shorter time between  $20^{\circ}$  and  $25^{\circ}$ ; it takes place also out of contact with air, and is excited even by yeast which has been boiled out with water. (Desfosses, *J. Pharm.* 15, 602; *N. Trs.* 21, 1, 159; *Schw.* 58, 98.) Under similar circumstances, lactic fermentation may likewise take place (comp. p. 277, 278).—On Mucous Fermentation, see also Vauquelin (*Ann. Chim. Phys.* 20, 93).

Water boiled with gluten produces in cane-sugar solution the same change as decoction of yeast. In contact with sugar-solution for 24 hours at  $25^{\circ}$ , it gives off a smaller quantity of gas than the decoction of yeast, and renders the liquid gummy. The gaseous mixture contains hydrogen in larger proportion to the carbonic acid than that which is evolved by decoction of yeast. After the completion of the mucous fermentation, the liquid is still very sweet, but so thick that it runs out in threads when the vessel is inverted; when evaporated, it leaves a non-crystallisable residue, and on treating this with alcohol, a sacchariferous gum remains undissolved. If the remainder of the sugar be extracted from the gum by fermentation with yeast, there are obtained, for every 100 pts. of sugar decomposed by the mucous fermentation, 109.48 pts. of a pale yellow insipid gum, which yields scarcely any mucic acid when treated with nitric acid, is less soluble in water than gum-arabic, and yields a thicker mucilage than the latter. (Desfosses.)

In the preparation of lactic acid by Bensch's process (xi. 475), there is obtained, together with mannite, a considerable quantity of a gum,

which, when the fermentation is complete, and the lactate of lime has been removed, may be obtained in a state of purity from the mother-liquor. This liquid is precipitated with sulphuric acid; the gypsum is removed; the filtrate is mixed with alcohol; and the precipitate is purified by repeated solution in water containing hydrochloric acid, and precipitation with alcohol. — It contains 43·61 p. c. carbon, 6·25 hydrogen, and 50·14 oxygen, turns the plane of polarisation to the right, reacts like arabic acid (p. 204) with cupric sulphate in alkaline solution, but does not yield mucic acid with nitric acid. (Brüning *Ann. Pharm.* 104. 197.)

*Combinations.*—*With Water.*—Cane sugar dissolves in  $\frac{1}{3}$  of its weight of water at mean temperatures, and in all proportions in boiling water. From a solution containing 5 pts. sugar to 1 pt. water,  $\frac{2}{3}$  of the sugar crystallises on cooling. (Henry, *J. Pharm.* 27, 8.) When 20 grms. of cane-sugar are dissolved in 100 cub. centims. of water, the temperature falls half a degree. (Dubrunfaut, *Compt. rend.* 23, 42.) When 0·56 kilog. cane-sugar is dissolved in 1·1 litre of water at 16·62°, the temperature falls to 15·5°. (Pohl, *J. pr. Chem.* 82, 154.) A concentrated solution, or syrup, of sugar is viscid, glutinous and ropy. On the expansion of sugar-solutions when heated, see Gerlach (*Kopp's Jahresber.* 1859, 48). — The specific gravity of cane-sugar solutions of definite percentage has been determined by Brandes & Reich (*Br. Arch.* 22, 70); Niemann (*Ann. Pharm.* 2, 341), Payen (*Dumas' Traité de Chimie appliquée*, 6, 256; *Gerhardt's Traité*, 2, 516); Brix (*Dingl.* 136, 214); Balling (*Gährungschemie*, Prag 1845, 1, 117, and *Suppl.* 81), and Steinheil (*Gehaltsprobe für Biere*, München, 1847). The most important of these tables, calculated by Pohl, are given in *Wien. Akad. Ber.* 11, 632 and *Handwörterbuch der Chemie* 7, 4.

*Percentage of Cane-sugar in Aqueous Solutions of different densities.*

(Extracted from the Tables of Balling and Brix).

Cane-sugar per cent.	Sp. gr. at 17·5°.	Cane-sugar per cent.	Sp. gr. at 17·5°.
1	1·0040	50	1·2165
5	1·0200	55	1·2610
10	1·0404	60	1·2900
15	1·0614	65	1·3190
20	1·0832	70	1·3507
25	1·1059	75	1·3824
30	1·1295	80	1·4159
35	1·1540	85	1·4499
40	1·1794	90	1·4849
45	1·2057	95	1·5209
		99	1·5504

When a solution of cane-sugar saturated at common temperatures is mixed with an equal volume of oil of vitriol, a stormy reaction sets in, heat is evolved, and the liquid froths up, giving off choking vapours of formic acid. Left to itself, it soon solidifies to a black humus-like mass, which, when mixed with 10 or 20 times its volume of water, gives a very strongly fluorescent liquid; the fluorescence is not destroyed by boiling, but immediately by neutralisation with bases. The solution contains an acid whose baryta-salt dries to a resinous mass (Simler, *Chem. Centr.* 1862, 378).

*With Bases.* — *Sucrate of Ammonia.* — 20 parts of pulverised sugar gradually absorb 1 pt. of ammonia-gas and form a dense tenacious mass, which smells of ammonia and gives it off on exposure to the air. (Berzelius.)

*Sucrate of Potash.* — An alcoholic solution of cane-sugar is precipitated with strong potash-ley; the semifluid precipitate is triturated with fresh alcohol, which renders it compact, and dried in vacuo, or in air free from carbonic acid. (Soubeiran.) White, friable translucent mass, shining on the fractured surface, melting at  $100^{\circ}$  to a viscid liquid, and having an alkaline, not sweet taste. (Brendecke.) According to Brendecke, it contains 12.6 p. c. potash, and consists of  $C^{24}H^{20}O^{20}, KO$  ( $C^{24}H^{20}O^{20}, KO = 12.41$  p. c.  $KO$ ). Soubeiran gives the same formula; Dubrunfaut (*Compt. rend.* 32, 498) gives  $C^{24}H^{20}O^{20}, KO$ . It turns brown when heated to  $110^{\circ}$ , and swells up strongly when heated. It is completely decomposed by a stream of carbonic acid, partially by air containing carbonic acid. — When its aqueous solution is exposed to the electric current, it gives off hydrogen at the negative pole, while an aqueous solution of carbonate of potash is formed at the positive pole. (Becquerel, *Ann. Chim. Phys.* 47, 5.) — It is not decomposed by aqueous boracic acid at mean temperatures. (Michaelis.) It is insoluble in pure alcohol, but dissolves in alcohol containing sugar. (Brendecke.) — A solution of cane-sugar loses 13 per cent. of its rotatory power on addition of 1 at. potash, but no more when a larger quantity of potash is added; hence there is probably but one definite compound of cane-sugar and potash. (Dubrunfaut, see also Michaelis, *J. pr. Chem.* 56, 411.)

*Sucrate of Soda.* — Obtained like the potash-compound, and exhibits similar reactions. (Brendecke, Becquerel, Dubrunfaut.) Contains 7.38 p. c. soda (Soubeiran), 8.2 p. c. (Brendecke). According to Soubeiran, it is  $C^{24}H^{20}O^{20}, NaO$ . ( $C^{24}H^{20}O^{20}, NaO = 8.52$  p. c.  $NaO$ .)

*Compound of Cane-sugar with Chloride of Sodium.* — On mixing the solutions of 1 pt. common salt and 4 pts. sugar, and leaving the liquid to evaporate, cane-sugar crystallises out first, and the mother-liquors, on further evaporation, yield this compound. — Small, sharp-edged crystals having a sweet and saline taste, deliquescing in the air. (Peligot, *Ann. Chim. Phys.* 67, 113.) In combination with common salt, cane-sugar retains its rotatory power unaltered. (Biot, *Compt. rend.* 15, 635.)

Belongs to the doubly oblique prismatic system, perhaps diclinohedral. The colourless crystals with rough, imperfectly reflecting faces are formed (*fig.* 125, without  $y$  and  $g$ ) from the two perpendicular dodecaïdal faces  $v$  and  $u$  whose edges are truncated by the hexaïdal faces (back and front), and  $x$  (right and left). The 8-sided prism thus formed is terminated above by a dihedral summit formed by the right dodecaïdal face  $k$  and the left  $h$ .  $x : z = 103^{\circ} 31'$  calc., =  $103^{\circ} 41'$  obs.;  $u : x = 136^{\circ} 15'$  calc., =  $136^{\circ} 17'$  obs.;  $u : z = 147^{\circ} 16'$  calc., =  $147^{\circ} 35'$  obs.;  $v : x = 116^{\circ} 14'$ ;  $v : z = 140^{\circ} 15'$ ;  $k : x = 129^{\circ} 4'$  obs.;  $k : h$  above =  $101^{\circ} 52'$  calc., =  $102^{\circ} 26'$  obs.;  $k : z = 98^{\circ} 2'$  calc., =  $97^{\circ} 55'$  obs.;  $k : u = 137^{\circ} 26'$  calc., =  $137^{\circ} 7'$  obs.;  $k : v$  behind =  $73^{\circ} 2'$  calc.;  $h : z = 81^{\circ} 58'$  obs.;  $h : u = 62^{\circ} 34'$ ;  $h : o = 106^{\circ} 35'$  calc. (Weiss, *Wien. Akad. Ber.* 37, 376.)



				Peligot.
24 C .....	144	...	36·7	36·8
21 H .....	21	...	5·3	5·7
21 O .....	168	...	43·1	42·8
NaCl.....	58·5	...	14·9	14·7
<hr/>				
$C^{12}H^{11}O^{11}, NaCl$ .....	391·5	...	100·0	100·0

So, according to Peligot. Graham splits the formula into  $C^{12}H^{11}O^{11} + C^{12}H^{10}O^{10}$ , NaCl. According to Gerhardt (*Traité* 2, 534), it is  $C^{24}H^{22}O^{22}, NaCl$ ; according to Blondeau de Carolles,  $C^{24}H^{20}O^{20}, NaCl, 3HO$ .

*Cane-sugar with Borax.*—Aqueous borax dissolves more cane-sugar than pure water. When a solution of cane-sugar saturated with borax is evaporated, borax crystallises out; and weak alcohol added to the mother-liquor, throws down a glutinous liquid, which, after repeated solution in a small quantity of water and precipitation with alcohol, contains 3 at. cane-sugar to 1 at. borax. The same compound,  $NaO, 2BO_3, 5HO + 3C^{12}H^{11}O^{11}$ , is obtained by dissolving the constituents in water and evaporating. (Stürenberg, *N. Br. Arch.* 18, 27.)

*Sucrate of Baryta.*—*Mono-acid.*—Obtained by the action of hydrate of baryta or monosulphide of barium on solution of cane-sugar, in the latter case with formation of sulphhydrate of barium—or by the action of sulphide of barium on sucrate of soda, with formation of sulphhydrate of sodium (Dubrunfaut, *Compt. rend.* 32, 498).—Baryta-water is heated to boiling with cane-sugar, the solution left to crystallise, and the crystals dried out of contact with the air (Brendecke, Peligot). The solution of 1 pt. baryta in 3 pts. water solidifies, when mixed with a 50 per cent. solution of cane-sugar, to a crystalline pulp, which does not redissolve when heated (Peligot).—Small nacreous crystals (Brendecke), resembling boracic acid, of caustic taste and alkaline reaction (Peligot).—The rotatory power of cane-sugar is not altered by baryta-water (Dubrunfaut).

The compound, after drying in vacuo, does not give off any water at 200°. (Peligot.) It is decomposed by carbonic acid, with separation of anhydrous carbonate of baryta (Pelouze, *Ann. Chim. Phys.* 48, 307).—It dissolves in 47·6 pts. of water at 15°; in 43·5 pts. water at 100° (Peligot, *N. Ann. Chim. Phys.* 54, 379). Insoluble in wood-spirit and in alcohol.

				Peligot.	Stein.	Soubeiran.
24 C .....	144	...	29·1	28·2	28·4	29·05
22 H.....	22	...	4·5	4·5	4·5	4·50
22 O .....	176	...	35·6	36·4	36·1	35·52
2BaO .....	153	...	30·8	30·9	31·0	30·93
<hr/>						
$C^{24}H^{22}O^{22}, 2BaO$ .....	495	...	100·0	100·0	100·0	100·00

So, according to Peligot, Pelouze, and Soubeiran. Compare Stein (*Ann. Pharm.* 30, 82; Peligot *N. J. Pharm.* 2, 103).

*Biacid?*—From the solution of cane-sugar in saturated baryta-water, alcohol throws down a precipitate containing 18·5 p. c. baryta. (Brendecke.) This precipitate contains cane-sugar in a state of mixture (Soubeiran).

*Sucrate of Strontia.*—The solution of equal quantities of sugar and strontia is pale yellow, has a caustic taste, and on cooling yields crystals which effloresce in the air from absorption of carbonic acid (Ramsey, *Schw.* 35, 488). Cane-sugar in combination with strontia

retains its rotatory power unaltered (Dubrunfaut).—Carbonic acid separates from the solution anhydrous carbonate of strontia (Pelouze).

*Sucrate of Lime.*—Lime dissolves in sugar-water (with evolution of heat, according to Peligot) in much larger quantity than in pure water (Lowitz). The quantity of lime which an aqueous sugar-solution is capable of taking up depends upon its density (Peligot, Berthelot) and temperature (Dubrunfaut).

100 pts. cane-sugar dissolved in water dissolve 55.6 pts. lime (Osann), 50 (Ure), 49.6 (Daniell), 29 to 30.6 (Hunton), 23 pts. forming  $\frac{2}{3}$ -sucrate of lime (Soubeiran). The sugar-solution at 100° takes up  $\frac{1}{4}$  at. lime to 1 at. sugar; at 0°, if it contains not less than 25 p. c. sugar, it takes up 2 at. lime to 1 at. sugar. (Dubrunfaut.) On the solubility of lime in sugar-solutions, Peligot formerly founded a mode of estimation of sugar (*Compt. rend.* 22, 936).

When a solution of sugar is agitated with excess of lime, complete saturation takes place but slowly, after repeated agitation, and only when the quantity of lime present is at least twice as great as that which the solution can take up. Solutions containing more than 30 p. c. sugar become gummy and then solidify; those which exhibit a density of 35° Bm. immediately form a sparingly soluble compound, not separable from the excess of lime. With somewhat more dilute solutions, monosucrate of lime is always formed, but this compound is capable of taking up an additional quantity of lime greater in proportion to the concentration of the solution. Sugar-solutions of 40 per cent. take up 26.57 pts. lime to 100 pts. sugar; solutions of 20 per cent. only 23.15 pts. and solutions of 5 per cent. only 18.06 pts., therefore more than 1.5 at. lime (exactly 1.62 at.) to 1 at. sugar, the monobasic sucate of lime formed in the first instance being partially converted into bibasic sucate. (Peligot.) Soubeiran supposes the solutions to contain  $\frac{2}{3}$ -sucrate, Berthelot  $\frac{3}{4}$ -sucrate of lime ( $3C^{12}H^{11}O^{11}, 4CaO$ ).

More dilute sugar-solutions containing not more than 2.4 p. c. sugar, dissolve less lime; moreover they dissolve a constant quantity which (after deducting the lime which the water itself dissolves) amounts to 12.6 pts. lime for 100 pts. sugar, corresponding apparently to the formulæ  $3C^{12}H^{11}O^{11}, 4CaO$ , requiring 10.91 p. c. lime. (Berthelot.) See Peligot's Table of the solubility of lime in sugar-water (*Compt. rend.* 32, 335; *N. Ann. Chim. Phys.* 54, 383); Berthelot's Table (*N. Ann. Chim. Phys.* 46, 176).

The aqueous solution of sucate of lime tastes bitter and alkaline but scarcely sweet. Its rotatory power is less than that of the sugar contained in it by 13 p. c. if 1 at. lime, by 26 p. c. if 2 at. lime have been added to 1 at. sugar (Dubrunfaut). On neutralising the solution with an acid, it recovers its rotatory power, even if it has previously been heated to 117.5°, but not if it has been heated to 119°. The presence of ferric oxide in the solution has no influence on these results. (Michaelis, *J. pr. Chem.* 56, 422).—The solution solidifies to a thick paste when heated, a large quantity of lime separating in combination with a small quantity of sugar (terbasic sucate according to Peligot), and becomes clear again on cooling (Osann, *Gilb.* 69, 292; *Kastn. Arch.* 3, 204). Part of the lime then remains dissolved, together with the greater part of the sugar (Osann), but the quantity of the latter retained in solution depends on the proportion of lime and sugar originally present, amounting to  $\frac{2}{3}$  of the original quantity, if the heated solution contained the monosucate, and

to half the original quantity if it contained the sesquibasic sucrate. (Peligot.) Dilute solutions of sucrate of lime become turbid at  $80^{\circ}$ ; concentrated solutions at  $100^{\circ}$ ; in highly concentrated solutions no precipitate is formed (Dubrunfaut). — When solutions containing  $\frac{1}{2}$  at. lime to 2 at. sugar are boiled continuously, no decomposition of the sugar takes place, not even such as would result from the boiling of its aqueous solution. (Dubrunfaut.) — When a cold-prepared solution of sucrate of lime has been decomposed by carbonic acid, no altered sugar can be detected in it by solution of copper; even if it has been boiled over the open fire for two hours, or till the boiling point has risen to  $120^{\circ}$  and the mass thickens and begins to char, the unburnt portion when treated with carbonic acid, still yields unaltered sugar. (Hochstetter *J. pr. Chem.* 29, 26.) The decomposition of sugar-solutions by boiling is retarded by the addition of chalk or of a small quantity of sucrate of lime, and does not take place at all in the boiling of saturated solutions of sucrate of lime. If however inverse sugar has been previously formed, this sugar is quickly decomposed by boiling (Soubeiran). — When solutions of sucrate of lime are evaporated there remains a colourless or pale yellow, translucent, viscid mass, which becomes friable when quite dry.

The solution of sucrate of lime, which remains unaltered if kept from contact with the air (p 261), deposits crystals of penta-hydrated carbonate of lime when exposed to the action of carbonic acid (or to the electric current, according to Becquerel, *Ann. Chim. Phys.* 47, 1), without (in the first case) any alteration of the sugar. (Pelouze, Brendecke.) Solutions of sucrate of lime become turbid on exposure to the air, only when they are dilute. (Kuhlmann, Dubrunfaut.) From the alcoholic solution, air containing carbonic acid throws down anhydrous carbonate of lime. (Brendecke.) — When carbonic acid is passed into a solution of monosucrate of lime, the liquid does not become turbid till the first third of the lime has been converted into carbonate; if the stream of carbonic acid be still kept up, the liquid solidifies to a jelly, the second third of the lime being then converted into carbonate, while the last third remains in solution as sucrate of lime, together with traces of carbonate. (Dubrunfaut.) According to Brendecke, the whole of the lime may be precipitated as carbonate. Lowitz (*Crell. Ann.* 1792, 1, 346). Daniell (*Ann. Chim. Phys.* 10, 221). Ramsay (*Schw.* 35, 488. — *Bibl. univ.* July, 1808). Franz Meyer (*Repert.* 7, 256). Brendecke (*N. Br. Arch.* 29, 75). Soubeiran (*N. J. Pharm.* 1, 469; *J. pr. Chem.* 26, 498; *Ann. Pharm.* 43, 223). Dubrunfaut (*Compt. rend.* 32, 498). Peligot (*Ann. Chim. Phys.* 67, 113; *Berz. Jahresber.* 19, 447), &c.

a. *Terbasic Sucrate of Lime.* — Separates on heating the aqueous solution of monosucrate of lime, or on heating a sugar-solution agitated with excess of hydrate of lime and filtered, as an opaque mass resembling coagulated white of egg, and is obtained by filtering the solution at the boiling heat, washing with hot water and drying at  $110^{\circ}$  in air free from carbonic acid. — It dissolves in more than 100 pts. of cold water, the solution when heated depositing half the quantity dissolved. It dissolves readily in sugar-water. (Peligot, *N. Ann. Chim. Phys.* 54, 379.)

					Daniell.	Peligot.
$C^{12}H^{11}O^{11}$ .....	171	....	67.06			
3 CaO .....	84	....	32.94	.....	33.52	..... 32.90
$C^{12}H^{11}O^{11}, 3CaO$ .....	255	....	100.00			

b. *Bibasic*.—Syrup of cane-sugar is digested with excess of hydrate of lime, the filtrate is precipitated with alcohol, and the precipitate is washed with alcohol and dried at 100°. (Hunton, *Phil. Mag.* [3], 11, 152; *J. pr. Chem.* 11, 409; *Berz. Jahresber.* 18, 321.)

				Hunton.
$C^{12}H^{11}O^{11}$ .....	171	....	69.79	
$2CaO$ .....	56	....	22.86	.... 22.65
$2HO$ .....	18	....	7.35	
<hr/>				
$C^{12}H^{11}O^{11}, 2(CaO, HO)$ .....	245	....	100.00	

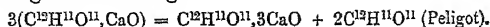
c. *Sesquibasic*.?—This compound is always formed when a solution of sugar is boiled or set aside at common temperatures, with excess of lime, and is obtained as a white amorphous gum by evaporating the filtrate out of contact with carbonic acid. (Soubeiran.) Brendecke moistens a mixture of equal parts of quicklime and cane-sugar with  $\frac{1}{2}$  pt. water, dissolves the resinous mass, which forms with rise of temperature, in cold water, and precipitates with alcohol, which throws down curdy flocks, or from concentrated solutions, tenacious clots. These are washed with alcohol and dried over oil of vitriol. Soubeiran uses 2 pts. of quicklime to 13 pts. of sugar.

Transparent, brittle resin, or granular, white, friable mass. Has a calcareous taste (Brendecke), nauseous (Soubeiran), and an alkaline reaction.—When very dry, it deflagrates quickly like gunpowder, on being heated. (Brendecke.)—It dissolves readily in cold water, separating out when heated (doubtless as terbasic sucate). It is insoluble in strong and in weak alcohol (Brendecke), but dissolves in an alcoholic solution of sugar. (Soubeiran.)

	at 100°.		Soubeiran. Brendecke.	
			mean.	
24 C.....	144	.... 33.80	..... 33.47	
22 H .....	22	.... 5.16	..... 5.16	
22 O .....	176	.... 41.32	..... 41.27	
3 CaO .....	84	.... 19.72	..... 20.10	.... 18.51
<hr/>				
$2C^{12}H^{11}O^{11}, 3CaO$ ....	426	.... 100.00	..... 100.00	

So, according to Soubeiran; according to Peligot, it is a mixture of bi- and monobasic sucates of lime.

d. *Monobasic*.—1. Solution of sugar is agitated with excess of hydrate of lime, filtered, and the filtrate is mixed with an additional quantity of sugar and precipitated with alcohol.—2. A concentrated solution of sugar is added by small portions to milk of lime till the whole of the lime is dissolved, and the solution is precipitated with alcohol of 85 per cent. (Brendecke.) Soubeiran uses in this case also 2 pts. quicklime to 13 pts. sugar.—White precipitate, becoming a brittle resin when dry. Deflagrates after drying, like tinder. (Brendecke.)—Dissolves easily, even after drying, in cold water (Brendecke), and the solution when heated deposits terbasic sucate of lime,—two-thirds of the sugar then remaining in solution,—and becomes quite clear again on cooling:



The precipitate disappears on adding cane-sugar, glucose, milk-sugar, or mannite to the hot liquid. (Brendecke.) Aqueous monobasic sucate of lime is capable of taking up a larger quantity of lime, being thereby

converted into sesquibasic sucrate (Soubeiran), partially into bibasic sucrate. (Peligot.) *vid. sup.*

					Soubeiran. <i>mean.</i>	Peligot.	Brendecke.
12 C .....	72	....	36.18	.....	36.38		
11 H .....	11	....	5.52	.....	5.48		
11 O .....	88	....	44.22	.....	43.74		
CaO .....	28	....	14.08	.....	14.40	.... 14.00	..... 14.3
$C^{12}H^{11}O^{11}, CaO$ .....	199	....	100.00	.....	100.00		

The presence of sugar promotes the absorption of sulphuretted hydrogen by milk of lime and the formation of *sulphydrate of calcium* (Dubrunfaut).

Sucrate of lime dissolves *carbonate of lime* (Barreswil, *Compt. rend.* 32, 469; *J. pr. Chem.* 53, 62; Dubrunfaut), only in traces. (Hochstetter, *J. pr. Chem.* 29, 28.) Solution of sucrate of lime gives no precipitate when mixed with chloride of calcium and carbonate of soda, but on adding a small quantity of sal-ammoniac the precipitate forms immediately. (Barreswil.)—Aqueous sucrate of lime dissolves *terbasic phosphate of lime*, either in the pulverised or recently precipitated state, the latter more abundantly. (Vasmer, *N. Br. Arch.* 24, 144; Bobierre, *Compt. rend.* 32, 859; *J. pr. Chem.* 53, 508.)—According to Larrey (*Gaz. medico di Milano*, Nr. 10, 1844) teeth immersed in a saturated solution of sugar become soft and gelatinous; but Marchand (*J. pr. Chem.* 40, 371) found teeth and bones unsoftened after lying in sugar-water for 14 days, the solution not containing a larger quantity of lime-salts than would have been dissolved by pure water. See also Heumann (*Repert.* 92, 321).

*Sucrate of Magnesia.*—The solution of magnesia in sugar-water is colourless and has a sweet taste; when kept in close vessels it deposits nearly all the magnesia in the course of a few months.

*Hydrate of Alumina* is very slightly soluble in sugar-water (Ramsey).—Aqueous cane-sugar does not dissolve *silicic acid* either in the amorphous or in the crystalline state. (Petzholdt, *J. pr. Chem.* 60, 368.)—Cane-sugar prevents the precipitation of *manganous salts* by potash-ley, the solution depositing peroxide of manganese when exposed to the air. (Lassaigne.) An aqueous solution of sugar does not dissolve sesquioxide of manganese (Peschier) or the peroxide. It does not dissolve *powder of algaroth*, and takes up only a small quantity of *antimoniac acid*. (Peschier.) It attacks metallic *zinc* when in contact with iron, but dissolves only inconsiderable quantities of pure zinc or *tin* (Gladstone, *Chem. Soc. Qu. J.* 7, 195).—Oxide of zinc does not dissolve in sugar-water (Peschier).

*Sucrate of Lead.*—Lead is attacked by cane-sugar solution in three days in warm weather, in a few hours at the boiling heat (Gladstone, *Chem. Soc. Qu. J.* 7, 195; *J. pr. Chem.* 64, 192).—Litharge dissolves in sugar-solution only when very finely pulverised; red lead more abundantly (Peschier, *J. Pharm.* 3, 510). Protoxide of lead forms with sugar an insoluble and a soluble compound (Berzelius). The latter is perhaps to be regarded as a solution of sucrate of lead in sugar-water (Kr). When sugar solutions are agitated with excess of lead-oxide, the whole of the sugar is precipitated as bibasic sucrate of lead, in crystalline needles (Dubrunfaut, *Compt. rend.* 32, 498).

*Bibasic.*—1. When sugar-water is boiled with litharge and the filtrate is left to stand for 24 hours out of contact with the air, white

flocks separate from it. (A. Vogel.) — 2. Lead-oxide is digested with solution of sugar in a closed vessel, as long as sugar is taken up by it (Berzelius, Mulder). — 3. Aqueous neutral acetate of lead is mixed with sugar-solution, ammonia is added, and the resulting gelatinous precipitate is dissolved in boiling water. The solution left to itself in a close vessel deposits nodules which may be dried in vacuo or over lime (Peligot). — 4. A solution of mono- or sesquibasic sucrate of lime is added to aqueous neutral acetate of lead, as long as the precipitate, which at first redissolves on agitation, continues to increase. (Soubeiran). — 5. Sesquibasic sucrate of lime is added to solution of neutral acetate of lead till the precipitate no longer disappears after forming, and the liquid is precipitated with alcohol (Soubeiran).

Crystalline needles or nodules, or white tasteless powder. When heated, it burns like tinder and leaves globules of lead. Insoluble in water whether cold or boiling, easily soluble in acids and in solution of acetate of lead. — If precipitated from sugar-solutions by neutral acetate of lead and ammonia, it does not change colour when heated (Schmidt, *Dissert. über Traubenzucker*, Götting. 1861).

				Peligot.		Mulder.	
				at 100°.		at 100°.	at 159°.
12 C	72	19.10	19.1	18.50	19.14		
9 H	9	2.38	2.4	2.69	2.50		
9 O	72	19.10	19.2	21.66	19.17		
2 PbO	224	59.42	59.3	57.15	59.19		
$C^{12}H^{10}O^{10}, 2PbO$				377	100.00	100.0	100.00

Contains 58.26 p. c. lead-oxide (Berzelius); when prepared according to 4 or 5, it contains from 58.6 to 59.5 p. c. (Soubeiran). Berzelius first assigned to it the formula  $C^{12}H^{10}O^{10}, 2PbO$ ; Peligot that above given. As Peligot originally examined the compound dried at 170°, Berzelius (*Berz. Jahresber.* 19, 443; *Compt. rend.* 8, 528) supposed that it contained sugar already altered (*caramel*), whereupon Peligot showed (*Compt. rend.* 8, 530) that the compound, dried at 100°, likewise possesses the above constitution, and contains unaltered sugar which may be recovered. According to Mulder (*J. pr. Chem.* 19, 187), the compound dried at 100° contains  $C^{12}H^{10}O^{10}, 2PbO$ , and does not become anhydrous till heated to between 141° and 143°, giving off 2.25 p. c. of its weight, and becoming somewhat coloured.

Cane-sugar mixed with inverse sugar behaves when shaken up with oxide of lead, in the same manner as pure cane-sugar. *a.* When 200 pts. of lead-oxide are mixed with 15 pts. cane-sugar and, as much water as is required to make up the mixture to 300 cub. cent., the lead-oxide, after two days' standing and agitation, takes up the whole of the sugar, so that the supernatant water contains no more of it. — *b.* If the same mixture contains inverse sugar instead of cane-sugar, the lead-oxide does not take up more than  $\frac{1}{20}$  of the sugar. — *c.* If the cane-sugar in *a* is converted, to the amount of  $\frac{1}{20}$  or more, into inverse sugar, the unaltered portion is likewise not taken up by the lead-oxide, or at least not completely. — *d.* If the mixture contains both kinds of sugar and less lead-oxide than *a*, the inverse sugar is almost wholly taken up, the cane-sugar only in part. In 200 cc. of a solution containing 10.66 grms. of each of the two sugars, and left for 14 days in contact with 100 grms. of lead-oxide, 0.14 grm. inverse sugar and 2.82 grms. cane-sugar still remained dissolved. The latter could not be crystallised after the removal of the lead, probably in

consequence of the admixture of glucic and apoglucic acid (Buignet, *N. Ann. Chim. Phys.* 61, 233).

Hydrated oxide of lead is dissolved by the sucrates of potash, soda, baryta and lime (Hunton).

*Cane-sugar with Iron.* — Ferrous oxide does not dissolve in sugar-water (Peschier), not even when recently precipitated (Gladstone). — Sugar-water has no action on ferric hydrate (Gladstone); it dissolves a small quantity of ferric oxide, precipitable by sulphide of ammonium, but not by ammonia, or by ferrocyanide of potassium (Peschier); it reduces ferric oxide to a slight extent when boiled with it. (Kuhlmann, *Compt. rend.* 49, 257.) — Pieces of iron, in contact with air, and with solution of sugar (especially if it contains salts) are rapidly corroded, while the portions wholly immersed in the liquid remain unaltered. The red-brown solution formed after 18 months' standing, leaves, when evaporated over the water-bath, a tasteless, insoluble residue corresponding to the formula  $FeO, C^{12}H^{11}O^{11}$ ; it is insoluble in alcohol, is precipitated by sulphide of ammonium, but not by the pure alkalis or their carbonates (Gladstone, *Inst.* 1854, 35; *Lieb. Kopp. Jahresber.* 1853, 537. — *Chem. Soc. Qu. J.* 7, 195; *Lieb. Kopp. Jahresber.* 1854, 619).

In a solution of sugar mixed with ferrous or ferric salts, potash-ley produces a precipitate which dissolves in excess of potash, forming a liquid which is either red-brown at first, or (in the case of ferrous salts) becomes so by contact with air (Lassaigne, Rose). Aqueous solution of sucrate of lime (potash, baryta, or strontia) dissolves sesquioxide of iron, converting it into protoxide. The residue left after evaporation and drying at  $100^{\circ}$ , contains 18 p. c.  $CaO$ , and 11.7  $FeO$ , corresponding to the formula  $C^{12}H^{11}O^{11}, 2CaO, FeO, 3H_2O$  (calc. 19.3 p. c.  $CaO$  12.4  $FeO$ ). The solution left in contact with the air, soon deposits crystals of carbonate of lime and ferrous carbonate: it is precipitated by alkaline succinates and benzoates, but not by pure alkalis or by ferrocyanide of potassium (Hunton).

*Cane-sugar with Cupric oxide.* — (See page 263.) — Sugar-solution dissolves perceptible quantities of copper when left in contact with it for some weeks in hot weather. (Gladstone.) — It does not dissolve cupric hydrate, except in presence of alkalis or alkaline earths. Cupric carbonate is abundantly dissolved by aqueous solution of sugar, the resulting green solution being precipitated by ferrocyanide of potassium and sulphide of ammonium, but not by alkaline carbonates. (Peschier, *J. Pharm.* 3, 510; *Repert.* 6, 85.) — A mixture of the concentrated solutions of cane-sugar and cupric sulphate, deposits, after standing for some time, a bluish white precipitate containing 1 at. sugar (therefore probably  $C^{12}H^{11}O^{11}$ ) to 1 at.  $CuO, SO_3$  and 4 at. water. This compound decomposes when its solution is heated with separation of cuprous oxide and metallic copper. When gradually heated alone, it gives off water and forms a lumsous substance. (Barreswil, *N. J. Pharm.* 7, 29; *J. pr. Chem.* 35, 253.)

Sucrate of potash, sucrate of baryta, and monosucrate of lime, do not of themselves dissolve cupric hydrate, but on adding more sugar the cupric hydrate dissolves immediately, forming a deep blue liquid. (Peligot.) Recently precipitated cupric hydrate dissolves abundantly in sugar-solutions mixed with potash, soda or lime, sparingly in such as contain baryta or strontia. (Becquerel, *Ann. Chim. Phys.* 47, 7.) —

When cupric hydrate in excess is mixed with sugar-solution and a small quantity of potash, the filtrate, which has a fine blue colour, leaves, on evaporation in vacuo, a transparent turpentine-like mass, containing 7.73 p. c. CuO, 8.83 KO, and 83.44 sugar and water. (Lassaigne, *J. Chim. méd.* 18, 820; *Berz. Jahresber.* 23, 280.)—Aqueous bibasic sucrate of lime dissolves cupric hydrate, forming a blue liquid, which, when evaporated in vacuo, leaves a crystalline mass, permanent in the air, and containing, after drying at 100°, 16.3 p. c. lime and 22.3 CuO, therefore  $C^{12}H^{11}O^{11}, 2CaO, 2CuO, 3HO$  (calc. 16.7 CaO and 23.9 CuO). Its solution heated to 70°, deposits blue flocks which redissolve completely on cooling. A similar effect takes place when the solution is boiled in an open, shallow vessel; but it decomposes, with separation of cuprous oxide, when heated once or twice in a test-tube, or after addition of sugar. (Hunton, *J. pr. Chem.* 11, 409.)

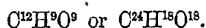
Cane-sugar solution does not attack metallic mercury, or metallic silver. (Gladstone.)

Cane-sugar dissolves in 80 pts. of boiling absolute alcohol, and separates out again almost completely on cooling (Pfaff); it dissolves in 4 pts. boiling alcohol of sp. gr. about 0.83, the greater part separating on cooling (Wenzel); in still weaker alcohol, sugar dissolves more abundantly, but not to so large an amount as in water. — Cane-sugar is precipitated in the crystalline form from its alcoholic solution by ether. (Döbereiner, *Ann. Pharm* 14, 249.)

Aqueous cane-sugar dissolves uric acid, which separates again on addition of hydrochloric acid. (Vasmer, *N. Br. Arch.* 24, 144.)

### *Appendix to Cane-sugar.*

#### 1. Caramelane.



GÉLIS. *N. Ann. Chim. Phys.* 52, 360; abstr. *Compt. rend.* 45, 590; *N. J. Pharm.* 32, 424; *Chem. Centr.* 1858, 163; *N. Br. Arch.* 95, 68; *Kopp's Jahresber.* 1857, 497.

See p. 248. The first product of the decomposition of cane-sugar by heat, and almost the sole constituent of the residue, if the loss does not exceed 10 per cent. The chief constituent of ordinary caramel.

To prepare it, caramel is immersed in alcohol of 84 per cent., which dissolves caramelane, unaltered sugar, and traces of caramelene, leaving caramalene and caramelin undissolved; the solution is evaporated; the unaltered sugar is decomposed by fermentation with yeast; the liquid is filtered and evaporated to dryness; the residue is treated with alcohol, which leaves caramelene undissolved; and the solution is evaporated.

Brown, inodorous, very bitter mass. Hard and brittle at mean temperature, semi-fluid at 100°.



<i>at 120°.</i>				Gélis.
12 C .....	72	....	47·06	..... 46·41
9 H .....	9	....	5·88	..... 6·53
9 O .....	72	....	47·06	..... 47·06
<hr/>				
$C^{12}H^9O^9$ .....	153	....	100·00	..... 100·00

Caramelane heated to 190° gives off water and is converted into carameline. — With *nitric acid*, it forms oxalic acid. — From an aqueous solution of *cupric oxide and potash* it throws down cuprous oxide, and from *gold and silver salts*, it throws down the metals. — Not fermentable with yeast.

Deliquesces in moist air, and dissolves readily in *water*, with fine gold-yellow colour. — The aqueous solution does not precipitate *metallic salts*.

*Barium-compound.* — Precipitated by a solution of baryta in wood-spirit added in excess to alcoholic caramelane. Contains 52·40 p. c. baryta, corresponding to the formula  $C^{12}H^8O^8, 2BaO$  (calc. 51·56 p. c.  $BaO$ ).

*Lead-compounds.* — a. *Bibasic.* — Ammoniacal sugar of lead added in excess to alcoholic caramelane throws down a precipitate containing 61 p. c.  $PbO$ , therefore  $C^{12}H^8O^8, 2PbO$  (calc. 60·76 p. c.  $PbO$ ). — b. *Monobasic.* — Separated from alcoholic caramelane by alcoholic sugar of lead, as a yellow precipitate, the liquid remaining coloured; purified by washing with alcohol.

				Gélis.
12 C .....	72	....	28·125	..... 28·81
8 H .....	8	....	3·125	..... 3·29
8 O .....	64	....	25·000	..... 25·70
$PbO$ .....	111·7	....	43·750	..... 42·20
<hr/>				
$C^{12}H^8O^8, PbO$ ...	255·7	....	100·000	..... 100·00

Caramelane dissolves in weak *alcohol*, slightly in absolute alcohol, not at all in *ether*.

## 2. Carameline.



GÉLIS. *N. Ann. Chim. Phys.* 52, 365.

Extracted by cold water from the residue insoluble in alcohol obtained in the preparation of caramelane from ordinary caramel. The solution is evaporated or precipitated with alcohol, and the admixed caramelin, which remains after dissolving in water and filtering, is removed. — If the loss of weight of the cane-sugar by heating amounts to about 15 per cent. the residue is rich in carameline.

*Properties.* Red-brown, hard, brittle mass, shining on the fractured surface. Permanent in the air.

	at 110°.			Gélis.
36 C .....	216	...	48·98	48·37
25 H .....	25	...	5·66	6·17
25 O .....	200	...	45·36	45·46
<hr/>				
$C^{36}H^{25}O^{25}$ .....	441	...	100·00	100·00

According to Gélis, it is  $3C^{12}H^8O^8 + HO$ .

With *nitric acid*, it forms oxalic acid. — It dissolves in dilute *acids*, the solution depositing red-brown flocks slowly in the cold, quickly when heated. It reduces *cupric oxide* in alkaline solution, also *nitrate of silver*.

Dissolves in *water*, with deep red-brown colour.

*Barium-compound*. — The solution of carameline in aqueous alcohol is mixed with excess of baryta-water, or a mixture of aqueous carameline with baryta-water is precipitated by alcohol.

				Gélis.
36 C .....	216·0	...	42·46	41·01
24 H .....	24·0	...	4·76	5·80
24 O .....	192·0	...	37·76	37·51
BaO .....	76·5	...	15·02	15·68
<hr/>				
$C^{36}H^{24}O^{24}, BaO$ .....	508·5	...	100·00	100·00

*Lead-compound*. — On precipitating *a*: Carameline mixed with excess of ammonia with sugar of lead; *b*: Aqueous carameline with ammoniacal sugar of lead; and *c*: A mixture of aqueous carameline and  $\frac{1}{2}$  alcohol with excess of alcoholic sugar of lead,—precipitates are formed containing: *a*, 61·8; *b*, 52·5; and *c*, 20·8 p. c. lead-oxide, therefore 1, 4, and 6 at. lead-oxide to  $C^{36}H^{24}O^{24}$ .

Carameline is easily soluble in aqueous *alcohol*, sparingly in absolute alcohol, insoluble in *ether*.

### 3. Caramelin.



GÉLIS. *N. Ann. Chim. Phys.* 52, 271.

Respecting Maumené's *Caramelin*, see page 262. — Contained in caramel, especially when the loss of weight of the cane-sugar amounts to 25 per cent. — Caramel, after exhaustion with alcohol of 84 p. c. and with cold water successively, consists chiefly of caramelin. This substance may occur in three different states, viz., as  $\alpha$ -caramelin, soluble in water, as  $\beta$ -caramelin, insoluble in water, but soluble in other solvents, and as  $\gamma$ -caramelin insoluble in all solvents. —  $\alpha$ . When the above-mentioned residue is boiled out with water, the  $\beta$ -caramelin partly dissolves as  $\alpha$ -caramelin, so that the solution deposits nothing on cooling, but yields with chloride of barium a precipitate of the barium-compound of  $\alpha$ -caramelin. —  $\beta$ . The solution when evaporated deposits black shining films of  $\beta$ -caramelin. When the above-mentioned residue is well boiled with aqueous alkalis,  $\beta$ -caramelin dissolves, and may be precipitated in

brown flocks by acids.— $\gamma$ . When  $\beta$ -caramelin is heated to  $110^\circ$ , or left in the moist state for several days, it is converted into  $\gamma$ -caramelin. (Gélis.)

$\alpha$ -Caramelin.—Known only in aqueous solution and in combination with baryta.

*Barium-compound of  $\alpha$ -Caramelin.*—Precipitated from aqueous caramelin by chloride of barium.

					Gélis. mean.
96 C .....	576.0	....	52.23	.....	51.20
50 H .....	50.0	....	4.53	.....	5.14
50 O .....	400.0	....	36.29	.....	36.28
BaO .....	76.5	....	6.95	.....	7.38
<hr/>					
$C^{96}H^{50}O^{50}, BaO$ .....	1102.5	....	100.00	.....	100.00

*$\beta$ -Caramelin.* Preparation and Properties, see above. Infusible, difficultly combustible mass, which forms oxalic acid with *nitric acid*, throws down cuprous oxide from an alkaline solution of *cupric oxide*, reduces the metals from *gold* and *silver salts*, and precipitates other metallic salts. Soluble in aqueous *ammonia* and in the *fixed alkalis*. Colours solutions 12 times stronger than caramelane. Soluble in aqueous, but insoluble in absolute *alcohol*.

*Barium-compound.*—Precipitated by chloride of barium from ammoniacal  $\beta$ -caramelin.—From alcoholic  $\beta$ -caramelin chloride of barium throws down a precipitate having the composition of the barium-compound of  $\alpha$ -caramelin.

					Gélis.
96 C .....	576	....	48.85	.....	48.35
50 H .....	50	....	4.24	.....	4.57
50 O .....	400	....	33.92	....	33.88
2BaO .....	153	....	12.99	.....	13.20
<hr/>					
$C^{96}H^{50}O^{50}, 2BaO$ .....	1179	....	100.00	.....	100.00

From aqueous  $\beta$ -caramelin, aqueous *sugar of lead* throws down a precipitate containing 9.8 p. c.  $PbO$ , corresponding therefore to the formula  $C^{96}H^{50}O^{50}, PbO$ .

*$\gamma$ . Caramelin.* See page 293. Insoluble in all menstrua. Forms oxalic acid with *nitric acid*.

					Gélis. mean.
96 C .....	576	....	55.65	....	55.08
51 H .....	51	....	4.92	....	5.06
51 O .....	408	....	39.43	....	39.86
<hr/>					
$C^{96}H^{51}O^{51}$ .....	1035	....	100.00	....	100.00

## 4. Nitrosaccharose.

SCHÖNBEIN. *Pogg.* 70, 100; abstr. *Pharm. Centr.* 1847, 505.

L. THOMPSON. *J. Chim. méd.* 24, 433. — *Pharm. J. Trans.* 8, 465;

*N. J. Pharm.* 15, 103; *J. Chim. méd.* 25, 69.

II. REINSCH. *Jahrb. pr. Pharm.* 18, 102; *Pharm. Centr.* 1849, 506.

A. & W. KNOP. *J. pr. Chem.* 56, 334.

*Nitrozucker, Nitrorohrzucker, Knallrohrzucker.*

*Formation.* By the action of fuming nitric acid (Sobrero, *Compt. rend.* 24, 247), of nitrosulphuric acid (Schönbein, Reinsch), on cane-sugar (p. 258).

*Preparation.* 1. One pt. pulverised cane-sugar is added to a mixture of 2 pts. oil of vitriol and 1 pt. mono-hydrated nitric acid, in which it at first remains suspended as a thin transparent pulp, then, if the liquid is continually stirred, cakes after a few minutes into a tenacious lump. This is washed with cold water, and kneaded in warm water till it no longer reddens litmus. (Schönbein.) — 2. One pt. pulverised cane-sugar is stirred up with a mixture of 16 pts. oil of vitriol and 6 pts. nitric acid of sp. gr. 1.5 cooled to 15°; the pasty mass, which separates after a few seconds, is washed with cold water, dissolved in alcohol, precipitated from the solution with excess of carbonate of potash, and purified by solution in ether and evaporation. (Thomson.) Thomson also uses 3 pts. oil of vitriol and 1 pt. nitric acid to 1 pt. sugar, allows the mixture to act upon the sugar for 4 minutes, then washes it, and boils for a few minutes with strong potash-ley. — Reinsch leaves the sugar for four hours in the cooled mixture of 3 vol. oil of vitriol and 2 vol. nitric acid of sp. gr. 1.52 (under which circumstances however it may take fire; p. 258), washes and dries it without application of heat.

*Properties.* White or transparent colourless resin, friable in the cold, but at mean temperatures, soft, glutinous, and capable of being drawn out into threads, having a silky lustre (Schönbein). Melts at about 30° (Reinsch). Inodorous. Tastes bitter. Neutral. Contains about 27 p. c. carbon, and 3 p. c. hydrogen. and is therefore  $C^{12}H^9X^2O^{11}$  (Sobrero; calculated 27.6 C. and 3.4 H).

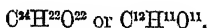
*Decompositions.* 1. *Heated* in an open vessel, it gives off aqueous vapour, then froths up and gives off hyponitric acid vapour, takes fire suddenly, and burns away leaving but little residue (Schönbein). Reinsch's nitrosaccharose explodes on red-hot platinum foil or under the hammer, deflagrates when touched with a glowing splinter, and, when heated in a porcelain crucible, melts, gives off red vapours and volatilises without explosion. — 2. Nitrosaccharose dissolves gradually in boiling water, the solution turning brown when evaporated, and leaving a bitter residue which is soluble in cold water, and when heated, first swells up and then detonates (Schönbein). — Nitrosaccharose kept under water in summer becomes soft, kneadable and glutinous, and after exposure to the air in the moist state, gives out when pressed, a liquid containing a considerable quantity of free nitric acid, without evolution

of nitrous vapours (Knop).—3. When gently heated with *oil of vitriol*, it dissolves, without colouring, but with an odour of nitric acid; from the bitter solution, which decolorises indigo, water separates nitric oxide gas, but does not form any precipitate even on addition of potash. At a higher temperature, the solution of nitrosaccharose in oil of vitriol gives off red vapours (Schönbein).—4. *Nitric acid* of sp. gr. 1.5 dissolves nitrosaccharose at  $24^{\circ}$  in all proportions, and the solution, which is precipitable by water, gives off hyponitric acid when heated, losing at the same time its bitter taste, and being then no longer precipitable by water (Schönbein).—5. When a solution of nitrosaccharose in ether-alcohol is boiled for several hours with an aqueous solution of *bisulphite of ammonia* completely saturated with sulphurous acid, the nitrosaccharose is completely decomposed, yielding carbonic acid, water, nitrous acid, and probably ammonia (Knop).—6. *Potash-ley* does not attack nitrosaccharose in the cold, but dissolves it with brown-red colour at a moderate heat. The solution is nearly decolorised by acids, and leaves a detonating residue when evaporated. See also Thompson's method of preparing nitrosaccharose (p. 294). Nitrosaccharose heated with sticks of potash, froths up, blackens, and then takes fire (Schönbein).—7. A mixture of the ether-alcoholic solution of nitrosaccharose with excess of *ammoniacal cuprous chloride* gives off a small quantity of gas when left to stand in sunshine, and decomposes when heated, like that with sulphite of ammonia above-mentioned (Knop).

Nitrosaccharose is insoluble in cold *water*, but melts to an oil in boiling water, and slowly dissolves. On cooling, the dissolved part separates out (Schönbein, Reinsch). The solution gives the reactions of nitrites (Schönbein).

It dissolves freely in *alcohol*, *ether*, and *fixed oils*. The alcoholic solution, when left to evaporate (or cooled), deposits crystals, according to Reinsch; none, according to Vohl (*Ann. Pharm.* 70, 360); a mass resembling turpentine, according to Schönbein and Thompson. The ether-alcoholic solution in certain proportions forms two non-miscible liquids (Knop).

### Melitose.



J. JOHNSTON. *Mem. Chem. Soc.* 1, 159; *Phil. Mag. J.* 23, 14; *J. pr. Chem.* 29, 485.

BERTHELOT. *N. Ann. Chim. Phys.* 46, 66; *Compt. rend.* 41, 392; *J. pr. Chem.* 67, 230; *Chem. Centr.* 1855, 699. *Chim. Organ.* Paris, 1860, 2, 260.

First recognised as a distinct substance by Johnston; further examined by Berthelot.—Occurs in manna from Van Dieman's Land, where the manna falls in opaque drops from various species of *Eucalyptus*.

*Preparation.* Crystallises by evaporation from the aqueous solution of manna, and separates abundantly on cooling from the hot

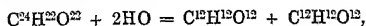
saturated alcoholic solution (Johnston). Berthelot purifies the aqueous solution with animal charcoal.

*Properties.* Hydrated melitose is obtained from the alcoholic solution in beautiful white, small, but well developed, crystals (Johnston); from water in thin microscopic interlaced needles (Berthelot). Tastes rather swcet. Dextro-rotatory power  $[\alpha]_D^{20} = 102^\circ$  for  $C^{12}H^{11}O^{11}$ ,  $= 88^\circ$  for  $C^{12}H^{11}O^{11}, 3HO$  (Berthelot). At  $100^\circ$  it gives off 2 at. and at  $130^\circ$  another 1 at. water, emitting at the same time a peculiar odour, and, being converted into anhydrous melitose, a pale yellow mass resembling barley-sugar (Berthelot). Melitose,  $C^{24}H^{22}O^{22}$ , crystallised from alcohol melts when quickly heated from  $94^\circ$  to  $100^\circ$ , giving off 11.23 p. c.  $= 5$  at. water (by calculation 11.36 p. c.); when slowly heated to  $82^\circ$  it yields in three hours 15.88 p. c.  $= 7$  at. water (by calculation 15.9 p. c.), without melting. Melitose fused at  $100^\circ$  scarcely decreases in weight at this temperature, and does not give up its 7 at. water completely till it is heated to  $115^\circ$ — $121^\circ$ , turning brown at the same time, from incipient decomposition, before the whole of the water is given off. If the 7 at. water are given off at a temperature not exceeding  $93^\circ$ , the anhydrous melitose remains in the form of a dry powder which begins to melt at  $138^\circ$ , and may be kept for several hours at  $149^\circ$  without turning brown or giving off water. It then absorbs moisture greedily from the air, and is converted into a syrup which gradually hardens to a colourless crystalline mass of the same weight as the crystallised melitose (Johnston).

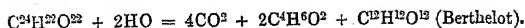
	at $100^\circ$		Berthelot.	
24 C .....	144	....	40.00	..... 39.6
22 H .....	22	....	6.11	..... 6.2
22 O .....	176	....	48.89	..... 50.6
2 HO .....	18	....	5.00	..... 3.6
<hr/>				
$C^{24}H^{22}O^{22}, 2HO$ .....	360	....	100.00	..... 100.0

According to Johnston, dried melitose  $= C^{24}H^{21}O^{21}$ . Vid. sup.

*Decompositions.* 1. When strongly heated, it emits an odour of caramel becomes carbonised, and burns away without residue. (Berthelot.)—2. When cautiously heated with moderately dilute nitric acid, it first forms a syrup, then a small quantity of mucic acid, and a larger quantity of oxalic acid.—3. Fuming hydrochloric acid at  $100^\circ$ , converts melitose in two hours into a black insoluble mass.—4. Melitose heated with dilute sulphuric acid, is resolved into equal parts of fermentable sugar and non-fermentable eucalin :



its rotatory power diminishing at the same time to about  $\frac{2}{3}$  of the original amount (Berthelot). The sugar is uncrystallisable, and behaves with alkalis, copper-solution, and in respect of its rotatory power, like grape-sugar. (Berthelot.)—5. Melitose ferments with yeast, yielding about half as much alcohol and carbonic acid (22.2 p. c.) as grape-sugar, together with non-fermentable eucalin :



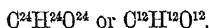
Melitose is not altered by boiling with aqueous alkalis, by heating to

100° with *hydrate of baryta* and a small quantity of water, or by boiling with *potassio-cupric tartrate*. (Berthelot.)

Melitose dissolves in water to about the same amount as mannite. The concentrated solution is not precipitated by alcohol. It forms a brownish precipitate with *baryta-water*, white with *ammoniacal sugar of lead*. (Johnston.) When melitose moistened with water is heated to 149° with oxide of lead, it gives off only 2 at. more water than when heated by itself, and is not further decomposed. The mass absorbs water greedily on cooling. When boiled with water, it yields a filtrate containing melitose, but no lead. (Johnston.)—It dissolves in boiling *alcohol* more abundantly than mannite.

### *Appendix to Melitose.*

### Eucalin.



BERTHELOT. *N. Ann. Chim. Phys.* 46, 72; *Chim. organ.* Paris 1860, 2, 250.

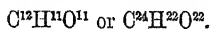
*Formation.* See 297. The liquid which remains after the complete fermentation of melitose is mixed with 4 or 5 vol. alcohol, and the filtrate is evaporated.

Slightly sweet syrup which retains 2 at. water in vacuo, and gives it up at 100°. Dextro-rotatory power about  $[\alpha]_j = 63^\circ$ .

	at 100°.			Berthelot.		
12 C .....	72	....	40.00	.....	39.5	
12 H .....	12	....	6.67	.....	6.5	
12 O .....	96	....	53.33	.....	54.0	
$C^{12}H^{12}O^{12}$ .....	180	....	100.00	.....	100.0	

Becomes coloured at 100°, and changes at 200° to a black insoluble mass.—With *nitric acid* it forms oxalic acid.—By *oil of vitriol* or *fuming nitric acid* at 100°, it is converted into humous substance.—*Dilute sulphuric acid* does not form any fermentable substance from eucalin.—Eucalin becomes coloured when heated with *baryta*.—It does not reduce *potassio-cupric tartrate*. It is not fermentable.

### Melezitose.



BONASTRE. *J. Pharm.* 19, 443 and 626; abstr. *Ann. Pharm.* 10, 337.

BERTHELOT. *N. Ann. Chim. Phys.* 46, 86.—*Compt. rend.* 47, 224; *J. pr. Chem.* 76, 188; *Ann. Pharm.* 108, 120; *Chem. Centr.* 1858, 673; *Rép. Chim. pure*, 1, 42 and 389. In detail *N. Ann. Chim. Phys.* 55, 282; abstr. *Kopp's Jahresber.* 1858, 488.—*Chim. organ.* 2, 266.

Discovered in the manna of Briançon, and recognised as a peculiar substance by Bonastre; investigated by Berthelot. — The manna of Briançon forms on young larches (*Pinus Larix*), also and more abundantly on the young twigs of old trees in hot dry summers. (Chancel, *J. Pharm.* 8, 355.) Respecting other exudates from various species of *Pinus*, see *Mannite*.

The extract of Briançon manna prepared with boiling alcohol deposits melezitose after being evaporated to a syrup, and left to stand for several weeks; the product may be purified by recrystallisation from boiling alcohol. (Berthelot.)

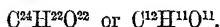
*Properties.* Very small, short, hard, shining crystals, resembling those of cane-sugar under the microscope, white and mealy when seen in mass; effloresces readily when exposed to the air, and gives off 4 p. c. of water when heated. Melts below  $140^{\circ}$  without further alteration, and solidifies to a glass on cooling. About as sweet as glucose. Dextro-rotatory power  $[\alpha]_D^{20} = 94.1^{\circ}$  for  $C^{12}H^{11}O^{11}$ . (Berthelot.)

	at $110^{\circ}$ .			Berthelot.	
12 C .....	72	...	42.10	.....	42.2
11 H .....	11	...	6.43	.....	6.6
11 O .....	88	...	51.47	.....	51.2
<hr/>					
$C^{12}H^{11}O^{11}$ .....	171	...	100.00	.....	100.00

*Decompositions.* Decomposed at about  $200^{\circ}$ . — Carbonises with cold oil of vitriol, quickly turns brown with boiling *hydrochloric acid*, and forms oxalic acid with *nitric acid*. — By an hour's boiling with *dilute sulphuric acid*, it is converted into glucose, more rapidly therefore than trehalose, but in longer time than is required for the inversion of cane-sugar. — In contact with *yeast*, it passes slowly or sometimes not at all, into vinous fermentation. It is not altered at  $100^{\circ}$  by aqueous *alkalis*, and scarcely by *potassio-cupric tartrate*. (Berthelot.)

Melezitose dissolves readily in *water*, and is precipitated by *ammoniacal sugar of lead*. (Berthelot.) — It is nearly insoluble in cold, slightly soluble in boiling alcohol, quite insoluble in *ether*. Absolute alcohol precipitates it from the aqueous solution. (Berthelot.)

## Trehalose.



BERTHELOT. *Compt. rend.* 46, 1276; *Inst.* 1858, 213; *J. pr. Chem.* 74, 291; *Ann. Pharm.* 108, 118; *Rép. Chim. pure*, 1, 389; *Chem. Centr.* 1858, 543. — *Compt. rend.* 47, 202; *J. pr. Chem.* 77, 1; *Ann. Pharm.* 109, 34. The two Memoirs in detail: *N. Ann. Chim. Phys.* 55, 272 and 291; abstr. *Kopp's Jahresber.* 1858, 486. — *Chim. organ.* Paris 2, 263.

Occurs in the Trehala manna of Syria. See Guibourt (*N. J. Pharm.* 34, 81; *Compt. rend.* 46, 1213); Hanbury (*N. Repert.* 8, 535).



*Preparation.* When pulverised trehala manna is treated with boiling alcohol, trehalose sometimes crystallises from the extract on cooling, sometimes not till after dilution and several days' repose. It is purified by washing with cold alcohol, boiling with small quantities of alcohol, and repeated crystallisation from boiling alcohol with help of animal charcoal.

*Properties.* Hard shining crystals, which grate between the teeth. They belong to the right prismatic system (Fig. 73). Rhombic prism  $u$ , whose obtuse angle =  $111^{\circ} 15'$  to  $111^{\circ} 46'$ ; bevelled above by the horizontal prism  $i$ . Inclination of  $i:i$  above =  $115^{\circ} 41'$  to  $116^{\circ} 11'$  (Berthelot). Not quite so sweet as cane-sugar. Air-dried trehalose heated to  $97^{\circ}$  loses 9.7 p. c. water, and at  $160^{\circ}$  neither gives off any more water nor melts—(calculation for  $C^{12}H^{11}O^{11}, 2HO = 9.5$  p. c. HO). When rapidly heated to  $100^{\circ}$ , it melts to a colourless glass which solidifies like cane-sugar on cooling. Dextro-rotatory power,  $[\alpha]_D^{20} = 220^{\circ}$  for  $C^{12}H^{11}O^{11}$ , =  $199^{\circ}$  for  $C^{12}H^{11}O^{11}, 2HO$ : scarcely altered by heat, and nearly as great in the recently prepared solution as in one which has been kept for 24 hours.

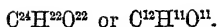
<i>Crystals.</i>				<i>Berthelot.</i>	
12 C.....	72	...	38.09	.....	38.2
13 H .....	13	...	6.88	.....	6.6
13 O .....	104	...	55.03	.....	55.2
<hr/>					
$C^{12}H^{11}O^{11}, 2HO$ .....	189	...	100.00	.....	100.0
<i>Dried.</i>				<i>Berthelot.</i>	
12 C .....	72	...	42.10	.....	41.9
11 H .....	11	...	6.43	.....	6.6
11 O .....	88	...	51.47	.....	51.5
<hr/>					
$C^{12}H^{11}O^{11}$ .....	171	...	100.00	.....	100.0

Differs from Mitscherlich's mycose (p. 301) only by its greater rotatory power (Berthelot). More recently (*Chim. organ.* 2, 263), Berthelot regards the two bodies as identical.

*Decompositions.* 1. Only partially decomposed between  $181^{\circ}$  and  $200^{\circ}$ ; carbonises when heated above  $200^{\circ}$ , giving off water, gases and an odour of caramel. — 2. Heated in contact with the air, it *burns* with a reddish flame. — 3. Heated with *nitric acid*, it yields oxalic, but no mucic acid. — 4. It is carbonised by heating with *oil of vitriol*, more slowly with fuming hydrochloric acid. — 5. By boiling for several hours with *dilute sulphuric acid*, it is converted into dextro-glucose. The transformation takes place much more slowly than the inversion of cane-sugar by acids; if the boiling be continued after it is complete (after 5 hours) the liquid becomes coloured. — 6. Trehalose heated with *acetic*, *butyric*, or *benzoic acid*, forms, under the same circumstances as dextro-glucose, saccharides, which are undistinguishable from those formed by dextro-glucose itself. — 7. In contact with *yeast*, it slowly and partially undergoes vinous fermentation. It is not altered at  $100^{\circ}$  by potash-ley, baryta-water or potassio-cupric tartrate.

Trehalose is very soluble in water, and crystallises from the aqueous solution evaporated to a syrup only after standing for some time. From the concentrated solution it is precipitated by ammoniacal *sugar of lead*. It is nearly insoluble in cold alcohol, but dissolves easily in *boiling alcohol*; insoluble in *ether*.

## Mycose.



WIGGERS (1833). *Ann. Pharm.* 1, 129; *Schw.* 64, 170.

MITSCHERLICH. *Berl. Akad. Ber.* 1857, 469; *J. pr. Chem.* 73, 65; abstr. *Ann. Pharm.* 106, 15; *Chem. Centr.* 1858, 93; *N. Ann. Chim. Phys.* 53, 232; *Chem. Gaz.* 1858, 123; *N. Cimento*, 7, 272; *Kopp's Jahresber.* 1857, 501.

*Ergot-sugar, Mutterkornzucker.*—Discovered by Wiggers, investigated by Mitscherlich. Liebig & Pelouze (*Ann. Pharm.* 19, 285) regarded mycose as identical with mannite.—It is perhaps identical with Berthelot's trehalose (p. 299). The mushroom-sugar (*Sucre des Champignons, Schwammzucker*), discovered by Braconnot, which, according to him, is found in *Agaricus piperatus* and *A. volvacius*, *Boletus juglandis*, *Peziza nigra*, *Merulius Cantharellus*, *Phallus impudicus*, and abundantly in *Hydnum repandum* and *H. hybridum*, is fermentable, crystallises easily in four-sided prisms, and is less sweet than cane-sugar. It has generally been regarded as mannite, since Liebig & Pelouze (*Ann. Pharm.* 19, 283), Knop & Schnedermann (*Ann. Pharm.* 49, 243), and Bolley (*Ann. Pharm.* 86, 44) demonstrated the general diffusion of mannite in fungi. As, however, Braconnot distinctly states that his mushroom-sugar is fermentable, and, on the other hand, Mitscherlich once found mannite in ergot of rye (another time he found neither mannite nor mycose), it is possible that a peculiar sugar may sometimes be present in fungi.—On the other hand, Vauquelin's sugar from *Agaricus theogalus* and *A. campestris* (*Ann. Chim.* 85, 5; *Schw.* 12, 253), Schrader's sugar from *Helvella mitra* (*Schw.* 33, 393), and Biltz's fungus-sugar (*Pilz-zucker*) from the husk of *Lycoperdon cervinum*, which, in the third edition of this Handbook, was regarded as mushroom-sugar, may with great probability be regarded as identical with mannite. Braconnot's *Mucoso-sucré* (*Ann. Chim.* 80, 273) from *Boletus pseudo-igniarius* does not appear to be a distinct substance (Kr).

*Occurrence.* In ergot of rye (Wiggers). Sometimes crystallises from the officinal extract (Kloboch, *N. Br. Arch.* 75, 135; 80, 13).

*Preparation.* The aqueous extract of pulverised ergot of rye is precipitated with basic acetate of lead; the excess of lead is removed from the filtrate by sulphuretted hydrogen; the filtered liquid is evaporated to a syrup; and the crystals which separate after a while are purified by washing with alcohol and recrystallisation from water (Mitscherlich). 2 kil. yielded 2 grm. mycose.

*Properties.* Hydrated mycose forms colourless transparent crystals of the right prismatic system, which separate from water with curved faces, from weak alcohol with plane highly lustrous faces. The dominant form is a rhombic prism (*Fig. 73*) of  $110^\circ 6'$  having its acute lateral edges bevelled by a rhombic prism which would form an angle of  $108^\circ 50'$  at the truncated edge; faces *t* and *m* subordinate. The prism is bevelled by the horizontal prism *i*; *i*:*i* above =  $160^\circ 32'$ ; faces of the octahedron and the horizontal prism *y* subordinate (Mitscherlich).

Tastes sweet. Inodorous. Neutral.—Dextro-rotatory power for  $\text{C}^{12}\text{H}^{11}\text{O}^{11} \cdot 2\text{H}_2\text{O}$ ,  $[\alpha]_D = 173^\circ 2'$  (Mitscherlich). Such is the value of  $[\alpha]$ , calculated according to Mitscherlich's statement, that 10.03 grms. of crystallised mycose produce a deflection of  $34.75^\circ$ ; from Mitscherlich's second statement (in the Memoir above referred to), that mycose deflects  $\frac{14.75}{1.333}$  times as strongly as cane-sugar, the value of  $[\alpha]$  should be  $192.5^\circ$ , therefore nearly as great as for trehalose (p. 299).

Mycose melts at  $100^{\circ}$  to a transparent mass, which on cooling solidifies first in the vitreous, afterwards in the crystalline form. Heated to  $130^{\circ}$ , it gives off 9.62 p. c. water (2 at. = 9.53 p. c.), and is converted into anhydrous mycose, which melts at  $210^{\circ}$  without further loss. (Mitscherlich.)

				Mitscherlich.
12 C	72	...	38.09	38.37
13 H	13	...	6.88	6.87
13 O	104	...	55.03	54.76
$C^{12}H^{10}O^{11}, 2HO$				100.00

For Liebig & Pelouze's analysis, see *Ann. Pharm.* 19, 285.

*Decompositions.* 1. Mycose when heated above  $200^{\circ}$  turns brown and gives off an odour of caramel, but, if then treated with water, crystallises partly unaltered. — 2. At higher temperatures and in contact with the air, it burns and leaves a spongy charcoal. — 3. *Nitric acid* of sp. gr. 1.52 dissolves it with slight evolution of heat, forming a solution from which water precipitates a gummy mass, soluble in alcohol and ether, insoluble in water, melting when heated and detonating with faint appearance of fire. (Mitscherlich.) By heating with ordinary nitric acid, it is converted into oxalic acid. (Wiggers, Mitscherlich.) — 4. It dissolves without decomposition in common and in fuming oil of vitriol, and turns brown when the solution is heated. — *Dilute sulphuric acid* boiled for some time with mycose converts it into dextro-glucose. — 5. The dark-blue solution produced by mixing *cupric sulphate* and potash-ley with mycose, deposits mere traces of cuprous oxide or none at all, even after prolonged boiling. (Mitscherlich.) Neither does any reduction to cuprous oxide take place on boiling mycose with cupric acetate. (Neubauer, *N. Br. Arch.* 72, 277; Kloboch.) — 6. According to Neubauer, mycose is fermentable.

Mycose dissolves easily in water. (Wiggers.) A solution containing 50 p. c. mycose does not crystallise on cooling. (Mitscherlich.) — It is not altered by aqueous *alkalis* (Wiggers) even after several hours' boiling. Not precipitable by *baryta-* or *lime-water* (Mitscherlich), by *metallic salts*, or *infusion of galls*. (Wiggers.)

It dissolves in more than 100 pts. of boiling alcohol and crystallises on cooling. It is insoluble in ether. (Mitscherlich.)

### Saccharoïdal Substances $C^{12}H^{10}O^{12}$ .

#### Indiglucin.



E. SCHUNCK. *Phil. Mag.* [4], 10, 73; abstr. *J. pr. Chem.* 66, 321; *Chem. Centr.* 1856, 50; *Kopp's Jahresber.* 1858, 659. — *Phil. Mag.* [4], 15, 183; abstr. *J. pr. Chem.* 74, 174; *Kopp's Jahresber.* 1858, 465.

*Formation.* Indican decomposes, when heated in the state of aqueous solution, or with dilute acids or aqueous alkalis, into indiglucin and other products. Similar products are yielded by indicanin, oxindicanin and oxindicasin. (See Indican.)

*Preparation.* 1. Tincture of woad-leaves, prepared with cold alcohol, is evaporated in a current of air; the residue is mixed with cold, very dilute sulphuric acid, and the fat which falls to the bottom is immediately separated by filtration. The filtrate serves instead of the aqueous solution of indican mixed with acids. The decomposition, which begins in the cold, is kept up by gentle heating, whereupon the solution becomes turbid, and a mixture of six insoluble substances separates (see Indican); the liquid is then filtered, the residue washed with cold water, and decomposed in the manner described under Indican. The filtrate, freed from sulphuric acid by carbonate of lead, and from lead by sulphuric acid, evaporated to a syrup in a stream of air, dissolved in alcohol, and mixed with a large quantity of ether, deposits leucine in crystals, and indiglucon as a syrup. The latter, after the removal of the crystals, is dissolved in water, the solution mixed with acetate of lead, the scanty precipitate removed, and the yellow lead-compound of indiglucon is precipitated from the filtrate by aqueous ammonia. The lead-salt decomposed by hydrosulphuric acid under water, treated with animal charcoal till a sample gives a white precipitate with ammoniacal sugar of lead, yields a solution from which, by evaporation, solution of the residue in alcohol, and addition of ether, the indiglucon is precipitated in the form of a syrup. 2. In the preparation of indicanin from indican, by mixing the latter with baryta-water and leaving it at rest, then removing the baryta, evaporating the filtrate in a current of air, dissolving the residue in alcohol, and precipitating by ether, indiglucon is separated as a syrup. This syrup is dissolved in alcohol, mixed with excess of alcoholic sugar of lead, the brown precipitate removed, and the solution precipitated with ammonia. The lead-compound of indiglucon is purified and decomposed as in method 1.

Colourless or light-yellow syrup having a slightly sweet taste.

*Decompositions.* 1. Swells up when heated and gives off an odour of caramel.—2. With boiling *nitric acid*, it forms oxalic acid.—3. With *oil of vitriol*, it becomes carbonised.—4. When boiled with *soda-ley*, it turns yellow and separates brown flocks.—5. From an *alkaline cupric solution* it reduces cuprous oxide; from an aqueous and still more from an *ammoniacal solution of nitrate of silver*, it reduces metallic silver; similarly with *terchloride of gold*.—6. It is not fermentable, but turns acid by prolonged contact with *yeast*.

Aqueous indiglucon dissolves *hydrate of lime*, and the solution on boiling deposits copious yellow flakes which dissolve on cooling and are precipitated by alcohol.—From a mixture of indiglucon with *baryta-water*, alcohol throws down yellow flakes.

*Lead-compound.* Aqueous indiglucon is precipitated by neutral or basic acetate of lead, only after addition of ammonia.

				Schunk.	
				a.	b.
				mean.	
12 C	72	...	11.67	...	12.74
9 H	9	...	1.46	...	1.64
11 O	88	...	14.26	...	15.85
4 PbO	448	...	72.61	...	69.77
$C^{12}H^9PbO^{18}, 3PbO$				617	...
				100.00	...
				100.00	...
				100.00	...

b. Prepared with baryta-water; in this product the composition of the organic substance after deduction of the lead-oxide, corresponds to the formula  $C^{12}H^9O^{11}$ . (Schunck.)

Indigluclin dissolves in *alcohol* and is precipitated by *ether*.

### Carbo-hydrates $C^{12}H^{12}O^{12}$ .

#### Dextro-glucose.



LOWITZ. *Crell. Ann.* 1792, 1, 218 and 345.

THÉNARD & DUPUYTREN. *N. Gehl.* 2, 195.

CRUIKSHANK. *Rollo "On Diabetes mellitus."* Lond. 1797.

PROUST. *J. Phys.* 63, 257; 69, 428. — *Ann. Chim.* 57, 131 and 225  
*N. Gehl.* 2, 77.

A. VOGEL. *Schw.* 5, 80; *Gillb.* 42, 123.

KIRCHHOFF. *Schw.* 14, 389.

SAUSSURE. *Ann. Chim. Phys.* 11, 381; *Schw.* 27, 304.

BRACONNOT. *Ann. Chim. Phys.* 12, 181; *Schw.* 27, 337.

DUBRUNFAUT (1823). *Ann. Chim. Phys.* 53, 73. — *Compt. rend.* 23, 38;  
*N. Ann. Chim. Phys.* 18, 99. — *N. Ann. Chim. Phys.* 21, 169; *J. pr. Chem.* 42, 418; abstr. *Pharm. Centr.* 1847, 889. — *N. Ann. Chim. Phys.* 21, 178; *J. pr. Chem.* 42, 425; abstr. *Compt. rend.* 25, 308;  
*Pharm. Centr.* 1848, 10. — *Compt. rend.* 29, 51; *Pharm. Centr.* 1849, 643. — *Compt. rend.* 32, 249; *Pharm. Centr.* 1851, 278; *Dingl.* 121, 299 (Estimation of Glucose). — *Compt. rend.* 42, 228; *J. pr. Chem.* 68, 422; *Chem. Centr.* 1856, 233. — *Compt. rend.* 42, 739. — *Compt. rend.* 42, 901; *J. pr. Chem.* 69, 438.

GUÉRIN-VARRY. *Ann. Chim. Phys.* 60, 54.

PELIGOT. *Ann. Chim. Phys.* 67, 136; *J. pr. Chem.* 15, 82; *N. Br. Arch.* 15, 227. Preliminary notice, *Compt. rend.* 7, 106; *Ann. Pharm.* 23, 169; *J. pr. Chem.* 12, 425; 13, 378; *Inst.* 1839, 237; *Berz. Jahresb.* 18, 279.

VENTZKE. *J. pr. Chem.* 25, 74.

SOUBEIRAN. *N. J. Pharm.* 1, 1; *J. pr. Chem.* 27, 281. — *N. J. Pharm.* 4, 347. — *N. J. Pharm.* 9, 327. — *Compt. rend.* 28, 775; in detail, *N. J. Pharm.* 16, 252; *J. pr. Chem.* 49, 65.

BERTHELOT. Combinations with Acids: *Compt. rend.* 41, 452; *J. pr. Chem.* 67, 235; in detail: *N. Ann. Chim. Phys.* 60, 95; abstr. *Rép. Chim. pure*, 2, 427. — Combinations with Tartaric and Citric acids: *Compt. rend.* 45, 268; *N. J. Pharm.* 33, 95; *J. pr. Chem.* 73, 157; *Chem. Gaz.* 1857, 441; in detail: *N. Ann. Chim. Phys.* 54, 74. — Fermentation with Chalk and Cheese: *Compt. rend.* 43, 238; *N. J. Pharm.* 30, 269; *J. pr. Chem.* 69, 454; *Chem. Centr.* 1856, 749; in detail: *N. Ann. Chim. Phys.* 50, 322. — Formation from Mannite and Glycerin: *Compt. rend.* 44, 1002; *N. J. Pharm.* 31, 432; *J. pr. Chem.* 71, 507; in detail: *N. Ann. Chim. Phys.* 50, 369. — *Chimie organique fondée sur la synthèse*, Paris, 1860, tom. 2.

E. BRÜCKE. Sugar in Urine: *Wien. Akad. Ber.* 28, 568; *J. pr. Chem.* 74, 108. — *Wien. Akad. Ber.* 29, 346; *J. pr. Chem.* 74, 115; *Chem.*

*Centr.* 1858, 705; *Rép. Chim. pure*, 1, 47. — *Wien. Akad. Ber.* 39, 10; *Chem. Centr.* 1860, 231; *Rép. Chim. pure*, 2, 219.

BUIGNET. *N. Ann. Chim. Phys.* 61, 233.

O. SCHMIDT. *Dissertat. über Traubenzucker*, 5c. Göttingen, 1861.

*Glucose, Ordinary Glucose; Krümelzucker*, and according to its origin; *Grape-sugar, Fruit-sugar, Honey-sugar, Starch-sugar, Diabetic sugar, Sugar of urine, Chestnut-sugar, Rag-sugar*, some of which names are also used to denote glucose in general. — Recognised as a distinct substance by Lowitz and Proust; first prepared from starch by Kirchhoff, from linen by Braconnot. Its combinations with bases have been investigated chiefly by Peligot; those with organic acids by Berthelot. Our knowledge of glucose has been further extended by Dubrunfaut, who has eliminated much that does not properly belong to it, and more exactly characterised its properties.

*Sources.* Impressions of ferns from the clay-slate of Petit-cœur, in Savoy, contain a sweet substance, which smells like caramel when burnt on charcoal, and perhaps consists of glucose. (Calloud, *Compt. rend.* 33, 544.) — On the alleged occurrence of sugar or dextrin in vegetable mould, see Verdeil & Risler (*Compt. rend.* 35, 97, and Petzhold's counter-statement, *J. pr. Chem.* 60, 368.)

*In the Vegetable Kingdom.* Abundantly in sweet fruits, frequently together with cane-sugar, and always with such a quantity of lævoro-rotatory fruit-sugar that the mixture may be regarded as inverse sugar (i. e., as produced by the decomposition of cane-sugar, p. 254) (Buignet, see page 239). — The isolated occurrence of dextro-glucose has been observed only in the following cases:

A thick viscid liquid which, in the summer of 1842, covered the upper surface of the leaves of lime-trees, and at certain times of the day fell down like rain, contained cane-sugar and dextro-glucose. (Biot, *N. Ann. Chim. Phys.* 7, 337; Langlois, *N. Ann. Chim. Phys.* 7, 348.) — Dextro-glucose is contained in the manna of the ash-tree; a false manna, of unknown origin, was found to contain a peculiar sugar not invertible by acids, and having a molecular rotatory power equal to  $\frac{2}{3}$  of that of cane-sugar; perhaps maltose (Biot, *Compt. rend.* 14, 49; *J. pr. Chem.* 27, 60). Whether the sugar occurring in many other parts of plants should be considered as dextro-glucose, is not yet decided. According to Buignet's researches (p. 240), cane-sugar and inverse-sugar (which may be regarded as a peculiar substance, at least with reference to its origin), appear to be the most widely diffused, and the imperfectly investigated granular sugar (*Krümelzucker*) of many chemists, appears to be inverse sugar formed either in the plant, or during the process to which it is subjected for the extraction of the sugar. (Kr.)

*In Honey.* This substance contains cane-sugar (which is gradually inverted by keeping); inverse sugar and an excess of dextro-glucose (Dubrunfaut, *Compt. rend.* 29, 51); comp. Soubeiran (*N. J. Pharm.* 16, 252) and page 240 of this volume.

*In the Animal body.* In many animal liquids and tissues; in the liver (*Handbuch viii, Zoochem.* 65), in the amniotic and allantoic liquids (*ibid.* 424) in the blood (*ibid.* 171 and 195), in the chyle (*ibid.* 221), in the transudates (*ibid.* 241), in the yolk and white of hens' eggs (*ibid.* 284 and 285). — In large quantity, to the amount of 8 or 10 per cent., in diabetic urine (*ibid.* 384), in small quantity also in the urine of healthy men (Brücke; Bence Jones, *Chem. Soc. Qu. J.* 14, 22; *N. Ann. Chim. Phys.*

62, 244; 65, 125). The urine of a fox fed exclusively on meat contained glucose. (Vintschgau, *Wien. Akad. Ber.* 42, 523.) Conjugated compounds of glucose are likewise found in the animal body. (See *Glucosides*.)

*Formation.* Of dextro-glucose and fermentable sugars in general isomeric therewith, in so far as they cannot with certainty be referred to other species. — A. *By the transformation of Carbo-hydrates with assumption of Water.* 1. Glucosan ( $C^{12}H^{16}O^{10}$ ; *vid. inf.*) is converted into dextro-glucose by boiling with dilute acids (Gélis). Assamar prepared by heating cane-sugar (p. 249), dissolved in water and set aside for  $1\frac{1}{2}$  years in a closed vessel, recovered the sweet taste of sugar, still more in two years, probably from conversion into glucose (Pohl, *J. pr. Chem.* 82, 148). Pohl's assamar doubtless contained glucosan. (Nicklès, *N. J. Pharm.* 39, 469.)

2. Dextrin is converted into dextro-glucose by boiling with dilute acids. (Biot & Persoz.) Diastase acts in like manner, according to Payen & Persoz, and Guérin-Varry; according to Musculus, it does not. See page 189, also on the intermediate products of the reaction, *infra*. 3. Under the same circumstances, soluble starch (p. 102) and common starch are converted into dextro-glucose, after they have been previously converted wholly or partially into dextrin, or other intermediate products. Dextro-glucose is also formed from starch by continued boiling with water, by prolonged contact with glutin, saliva, or the nitrogenous and animal matters mentioned on page 91, and from sulphamidonic acid by heating its aqueous solution (p. 104).

On the change which takes place in the conversion of starch into dextro-glucose, the following views have been proposed.

a. According to Kirchhoff, the starch is directly converted into glucose. — b. According to Biot & Persoz, when a mixture of 500 pts. starch, 120 pts. oil of vitriol, and 1,390 pts. water is heated to  $90^{\circ}$  —  $95^{\circ}$  (under the circumstances mentioned at page 85), or till a clear solution is produced, dextrin is formed, which, when the temperature has risen a few degrees, is converted, with sudden diminution of the rotatory power of the solution, into a peculiar dextro-rotatory sugar, and by continued boiling, into dextro-glucose. With other proportions of water, acid, and starch, the same changes take place, but more or less quickly and at other temperatures. The first-formed sugar is, according to Dubrunfaut, maltose. The dextrin of Biot & Persoz, appears to have been a mixture of disorganised with soluble starch, dextrin and dextro-glucose (or maltose), since it had a greater rotatory power than dextrin, less than soluble starch, *viz.*  $[\alpha]_D = 175.7^{\circ}$ , was coloured purple by iodine, was fermentable (hence the statement of Biot & Persoz, p. 188, requires rectification), and when kept in aqueous solution deposited a white powder, which Jacquelin (*Ann. Chim. Phys.* 73, 177) afterwards regarded as identical with his *Granules de fécule*. The amount of sugar was previously ascertained by Guérin-Varry (*Ann. Chim. Phys.* 56, 239 (Kr.).

c. According to Payen & Persoz, who distinguish between the integuments of the starch-granules, amounting to  $\frac{1}{2}$  p. c., and the contents, amounting to 99.5 p. c. (designating the latter as *amidone*), diastase or malt heated with starch and water causes the contents of the granules to separate out, part of the substance remaining for a short time in the liquid without alteration, and being subsequently converted into dextrin and sugar, the diastase, however, not being able to pro-

duce any further alteration of the dextrin, even after the sugar has been removed. The amidone of Payen & Persoz appears to be identical with disorganised or soluble starch, but their dextrin is different from that of Biot & Persoz, inasmuch as it is not coloured by iodine (*Ann. Chim. Phys.* 53, 73; 56, 337). More recently, Payen states (*Ann. Chim. Phys.* 60, 442) that starch is completely converted into sugar by diastase, with the exception of the integuments. According to Mulder (*Chimie des Bieres*, 170) the dextrin produced by diastase is different from that which results from the action of acids, as appears also to follow from Guérin-Varry's statements (*Ann. Chim. Phys.* 60, 32), but both diastase and acids appear to produce successively the dextrin which is coloured purple-red by iodine and that which is not coloured. (Kr.)

d. According to Jacquelin, who likewise distinguishes in the starch-granule an envelope and a granular substance contained therein, the first effect of heating starch with water to  $150^{\circ}$ , is to separate these two constituents, the envelopes remaining undissolved, while the granular contents, Jacquelin's *Granules de fécule*, dissolve. [The characteristic property of the *granules de fécule* is, that they separate out, for the most part, when the aqueous solution is left to cool, dissolve sparingly in cold water, but easily in water at  $70^{\circ}$ , are coloured blue by iodine, and are precipitated from their aqueous solution by alcohol much more easily than dextrin. They appear therefore to be identical with Béchamp's disorganised starch (p. 102)]. The *granules de fécule*, when further heated with 5 pts. water to  $160^{\circ}$  are converted in  $\frac{3}{4}$  hour into  $\alpha$ -dextrin (which is coloured purple by iodine, and is more easily precipitated by alcohol than  $\beta$ -dextrin), in  $1\frac{1}{2}$  hour into  $\beta$ -dextrin (not coloured by iodine), and by still further heating, into sugar. At higher temperatures, the same products are formed, but are more quickly converted into the last-mentioned compound. When starch is heated with an equal weight of water and from  $\frac{3}{1000}$  to  $\frac{5}{1000}$  of oxalic acid, or oil of vitriol, to  $130^{\circ}$ , the mass, after 20 minutes, contains  $\alpha$ -dextrin, after an hour,  $\beta$ -dextrin, and after 2 hours, sugar. (Jacquelin, *Ann. Chim. Phys.* 73, 167.) The sugar formed in this reaction possesses, according to Biot (*Compt. rend.* 15, 619 and 710; 42, 351) a molecular rotatory power different from that of dextro-glucose, viz.  $[\alpha]_D = 100.6^{\circ}$  to the right, because, according to Dubrunfaut, it is a mixture of maltose and dextro-glucose (see *Maltose*).

e. According to Neubauer, dilute acids produce first Schulze's amyduin, from this  $\alpha$ -dextrin, which is coloured purple-red by iodine, then  $\beta$ -dextrin, not coloured by iodine, and, finally, after very long boiling, a solution containing nothing but glucose.

f. According to Béchamp, the formation of sugar from starch by dilute acids, is preceded—just as when diastase is the acting substance,—by the formation of three different products, whilst a fourth appears either before the sugar, or simultaneously with it. These products, some of which may be isolated by the use of aqueous alkalis or of concentrated acids, are as follows:  $\alpha$ . *Disorganised starch*, occurring in three forms, in one of which it constitutes Jacquelin's *granules de fécule*, in another Saussure's *Ligneux amylicé*; —  $\beta$ . *Soluble starch* (p. 102) which is coloured blue by iodine, dissolves in cold and in hot water and does not separate from the latter solution on cooling; —  $\gamma$ . *Dextrin*,



which is not coloured blue (but purple-red? Kr.) by iodine;—  
 d. A variety of dextrin, Béchamp's *Amylin*, which is formed, either together with or before the sugar, often remains mixed with it, and has a dextro-rotatory power  $[\alpha]_D = 125^\circ$ . (Béchamp, *N. Ann. Chim. Phys.* 48, 458). The presence of Béchamp's *Amylin* (or Jacquelin's  $\beta$ -dextrin) appears also to explain the observation made by Anthon (*Dingl.* 151, 213; *Chem. Centr.* 1859, 291), that, by boiling starch with water and 2 p. c. oil of vitriol for 5—7 hours, a solution is obtained which is not coloured by iodine or precipitated by alcohol, but does not yield any crystals by evaporation, and ferments only to the amount of  $\frac{2}{3}$  to  $\frac{3}{4}$  of its entire quantity.

g. According to Musculus, dilute acids and diastase decompose starch into 2 at. dextrin and 1 at. dextro-glucose, the former being afterwards but slowly altered by dilute acids, and not at all by diastase. This does not agree with Guérin-Varry's experiments (pp. 90 and 91), in which the quantity of sugar obtained was much larger than that which corresponds to the equation given by Musculus. Neubauer (*N. Br. Arch.* 72, 285), appears to have converted starch completely into sugar by the action of diastase; the quantity of product obtained in the brandy-distillery, shows that the sugar produced by the action of malt upon starch amounts to between 75 and 80 p. c. of the weight of the starch; and, finally, Guérin-Varry states distinctly (p. 188) that he converted dextrin into sugar by the action of diastase, not however till the sugar first formed was removed. From this, as well from experiments of my own, the view proposed by Musculus appears to me to be untenable (Kr.).

Lastly, there are certain observations by Gentile (*Dingl.* 158, 427; *Chem. Centr.* 1861, 91), which indicate the formation of another intermediate product: When starch is boiled with dilute acids till the mixture remains clear on cooling, the presence of glucose in it is shown by potassio-cupric tartrate, but not by red prussiate of potash mixed with caustic potash, which reagent is nevertheless decolorised by glucose.

In the spontaneous decomposition of starch-paste, there is obtained, amongst other products, a sugar, which, according to Saussure, resembles grape-sugar, and according to Dubrunfaut, is maltose. When a paste prepared with 1 pt. starch and 12 pts. water is exposed to the air for two years in a shallow vessel, and the mass is then exhausted with cold water, undecomposed starch, woody starch (Saussure's *ligneux amylicé*) and a small quantity of resin remain undissolved, while amidin, starch-gum, and sugar pass into the solution. On evaporating the filtrate, dissolving the residue in 1 pt. of water, adding 10 pts. alcohol, evaporating again, and separating the remainder of the matter insoluble in alcohol, an alcoholic solution is obtained from which, after evaporation, the sugar crystallises. If the spontaneous decomposition of the starch-paste continues only a few weeks, sugar is likewise formed, but of the uncrystallisable kind; if the decomposition has proceeded too far, the crystallisable sugar also disappears. This crystallisable sugar dissolves in 8 pts. alcohol of  $35^\circ$  Bm. at  $25^\circ$ , and in 17 to 20 pts. of boiling absolute alcohol (Saussure, *Ann. Chim. Phys.* 11, 379).

4. Glycogen is converted into dextro-glucose under the same circumstances as starch (p. 184).—5. In like manner, lichenin (p. 121)

and paramylone (p. 122) are converted into glucose by boiling with acids. The rotatory power of the sugar has not been ascertained in either case.

6. Cellulose treated with oil of vitriol (p. 136), concentrated hydrochloric acid (p. 139), or a concentrated aqueous solution of chloride of zinc (p. 140), yields products which are converted into glucose when their aqueous solution is boiled with water. — Glucose is likewise produced in the decomposition of liguosulphate of lead (p. 165), and by the action of alkalis on pyroxylin (p. 178). But it is doubtful also whether this sugar should be regarded as dextro-glucose. According to Béchamp (*N. Ann. Chim. Phys.* 48, 502), it yields, when treated with alcohol, two sorts of crystals, one sort having the hardness of cane-sugar, the others resembling dextro-glucose.

The skin of the silk-worm and that which remains in the cocoons when the butterflies escape, are capable of yielding a substance isomeric with cellulose, which may be converted into glucose. When the caterpillars are boiled for several hours with strong hydrochloric acid, and this treatment is repeated three times with the residue, and this residue is washed with strong potash-ley, then with water, and dried between  $100^{\circ}$  and  $110^{\circ}$ , a white light substance nearly free from nitrogen is obtained, which gradually diffuses in oil of vitriol, forming a colourless gummy liquid. This solution added by small quantities to boiling water and boiled for an hour or two, yields fermentable sugar which reacts, like glucose, with common salt and potassio-cupric tartrate (De Luca, *Compt. rend.* 53, 102).

7. Tuicin (p. 182) is decomposed by oil of vitriol, under the same circumstances as cellulose, into dextro-glucose and a second substance. (On the decomposition of Chitin, see *Glucosides*.)

8. Maltose (p. 339), melezitose (p. 299), trchalose (p. 300) and mycose (p. 301) are completely converted into dextro-glucose by boiling with dilute acids.

B. Another class of compounds yield by their decomposition, dextro-glucose and another product. This latter body is either isomeric with glucose: thus melitose (p. 297) is resolved, by dilute acids, yeast, and other bodies, into dextro-glucose and eucalin, — cane-sugar (p. 251), into dextro-glucose and levo-glucose (as to starch, dextrin, and tuicin, it is doubtful whether they belong to this or to the former class); or, it belongs to the class of non-saccharine bodies, in which case the compound which yields this second product and dextro-glucose, belongs to the class of *Glucosides*.

To the *Glucosides*, *Glucosanides*, or *Saccharogens* belong, according to Laurent's classification (*N. Ann. Chim. Phys.* 36, 330), all substances which, when decomposed by dilute acids, yield, on the one hand, dextro-glucose or another saccharine substance, on the other, a product differing in character according to circumstances, but not belonging to the carbo-hydrates. Generally speaking only the naturally occurring compounds of this kind, the *Bitter principles*, are designated by this name. Berthelot's *Saccharides* (p. 317) include, besides these, the artificially prepared compounds of the carbo-hydrates (with acids), and are divided, according as they yield by their decomposition, dextro-glucose, levo-glucose, lactose, or other bodies of like nature, into glucosides, levulosides, gallactosides, &c. But since, in many cases, decisive experiments on the nature of the saccharine substance obtained are wanting, Berthelot's classification cannot be completely carried out, and we shall therefore adhere to Laurent's. (Kr.) See the *Conspectus of the Glucosides*, in the *Appendix to the Carbo-hydrates*.

C. In the decomposition of dulcitol ( $C^{12}H^{14}O^{12}$ ) by nitric acid, there is formed, amongst other products, a sugar,  $C^{12}H^{12}O^{12}$ , which reacts

with alkalis, potassio-cupric tartrate, basic nitrate of bismuth, and indigo, in the same manner as dextro-glucose. (Carlet, *Compt. rend.* 51, 137.)—Respecting Gorup-Besanez' *Mannitose*, a sugar different from dextro-glucose produced by the oxidation of mannite ( $C^{12}H^{14}O^{12}$ ) under the influence of platinum-black, see *Mannite*.

D. *From Oxalate of Ethyl*.—When this compound is brought in contact with sodium-amalgam at low temperatures, and the product is agitated with ether, a solution is obtained from which a greasy mass separates on addition of water. This mass is a mixture of oxalate of soda, another soda-salt, and fermentable sugar. (Löwig, *J. pr. Chem.* 83, 133.) Whether this sugar should be regarded as dextro-glucose is at present undecided. (Kr.)

E. *From Mannite or Glycerin*.—When a moderately concentrated aqueous solution of mannite, dulcitol, or glycerin is left for some time in contact with the testicles of man, or of the horse, dog, or cock, a peculiar fermentable sugar is produced, the formation of which likewise takes place in certain cases, when instead of the testicle, albumin, casein, fibrin, gelatin, or the tissue of the kidneys or pancreas is employed. (Berthelot, *N. Ann. Chim. Phys.* 50, 369.)

When to a solution of mannite or glycerin in 10 pts. water, there is added such a quantity of comminuted testicle, that its dried substance amounts to  $\frac{1}{10}$  of the mannite, and the mixture, contained in an open flask, is exposed to diffused daylight between  $10^{\circ}$  and  $20^{\circ}$ , the liquid, after an interval varying from a week to 3 months, is found to contain (without the occurrence of putrefaction, which, indeed, is incompatible with the success of the experiment) a substance which reduces cupric tartrate. The testicular tissue, if separated at this time from the liquid by decantation and thorough washing, then again introduced, under similar circumstances, into a solution of mannite or glycerin, produces therein, in the course of a few weeks, a considerable quantity of sugar. This sugar is formed, sometimes in extremely small, sometimes in larger quantity, amounting to  $\frac{1}{10}$  of the mannite or glycerin, and is partly further altered during the operation. It is not formed by the substance of the testicle, inasmuch as this substance is recovered, for the most part, unaltered, and gives up to the liquid, chiefly salts and albuminoidal substances, amounting to less than the weight of the sugar.—The sugar is probably lævo-rotatory. It is deliquescent, uncrystallisable, and cannot be separated from the glycerin. It is apt to alter during the evaporation of its solution, is turned brown by alkalis, easily fermented by yeast, and reduces potassio-cupric tartrate. It is very soluble in water, alcohol, and glycerin, and slightly precipitable by ammoniacal sugar of lead. (Berthelot.) On the formation of sugar in the muscles and lungs of the foetal calf, see *Handbuch*, viii, *Zoochem.* 489.

Pectin, pectic acid, and pectous acid are converted into sugar, according to Chodnew, by boiling with dilute acids, a statement which is contradicted by Frey. Apiin, according to Braconnot, exhibits a similar reaction; according to Planta & Wallace, it does not. Bassorin (p. 208) and vegetable mucilage (p. 211), treated in like manner, yield a sugar, which cannot with certainty be reckoned as belonging to this place.—The following substances were formerly erroneously regarded as dextro-glucose:—The inverse sugar produced by inversion of cane-sugar (p. 254),—the lævo-rotatory fruit-sugar produced from inulin,—lactose (p. 227),—the sugar, probably identical with lactose, produced from arabic acid,—and maltose. The observations of Biot (*Compt. rend.* 15, 619; 15, 710; 42, 351), who found that the sugar which Jacquelin obtained by heating starch with oxalic acid (pp. 87, 307), also the sugar examined by Peligot, and the

dextro-glucose of the manufactories, exhibited different degrees of dextro-rotatory power (viz.  $[\alpha]_D^{20} = 100.6^\circ$ ,  $61.5^\circ$ , and  $51.4^\circ$ ), must for the present remain unexplained, so far at least as the two latter products are concerned.

*Preparation.* 1. *From the juice of various kind of fruit, especially of Grapes.* The juice is boiled and skimmed; the free acid is neutralised with chalk or marble; and the liquid is concentrated to one-half, clarified by deposition and decantation, or further with white of egg, and evaporated to a syrup, not too thick. From this the grape-sugar separates after some weeks, and is purified by repeated solution in water and crystallisation.

2. *From Honey.* White granular honey is diffused in  $\frac{1}{2}$  pt. of cold strong alcohol, which dissolves the more soluble levo-glucose and leaves the dextro-glucose for the most part undissolved; the solution is separated from the sediment after a few hours; the sediment strongly pressed; the residue again triturated with  $\frac{1}{10}$  pt. alcohol; again pressed; and the undissolved portion is purified by solution in water and crystallisation. (Braconnot, *Bull. Pharm.* 3, 360.) A similar process is followed by Proust, also by Cavezzalli (*Scher. J.* 7, 714), and Trommsdorff (*N. Tr.* 9, 1, 287). — 2. Siegle spreads granular honey on dry porous bricks, whereby the liquid portion is absorbed, leaving, after a few days, a granular residue, which is recrystallised from warm alcohol with help of animal charcoal. (*J. pr. Chem.* 69, 148.) The dextro-glucose obtained by either of these processes must be contaminated with cane-sugar, if the honey contained that substance. (Kr.) See also Clerget (*N. J. Pharm.* 16, 252).

3. *From Starch by the action of dilute Sulphuric acid.* — 1 pt. of starch is boiled with 4 pts. water and a quantity of oil of vitriol, weighing from  $\frac{1}{100}$  to  $\frac{1}{10}$  as much as the starch, the liquid being stirred and the water continually renewed till the liquid is no longer precipitated by alcohol. To bring it to this state, the boiling must be continued for a longer time in proportion as less sulphuric acid has been used; with the above proportions, from 6 to 36 hours' boiling is required. The dextro-glucose then contained in the solution is separated and purified in the same manner as that from grape-juice. (Kirchhoff.) In preparing starch-sugar on the large scale, the ebullition is produced by passing over-heated steam into the mixture contained in closed casks. — When starch is boiled with water and 2 p. c. oil of vitriol, the liquid being evaporated after 5 or 7 hours, at which time it is no longer precipitated by alcohol, an uncrystallisable syrup is obtained. It is only after longer boiling that the whole of the dissolved matter is converted into dextro-glucose, part of which moreover undergoes further alteration, so that the liquid does not easily yield crystals by evaporation. (Anthon, *Dingl.* 151, 213.) After the sulphuric acid has been neutralised with chalk, a small quantity of acetic acid must be added before boiling the liquid, since an excess of lime leads to the formation of bitter products of decomposition (*Polyt. Centr.* 1854, 252); see also Payen (*Repert.* 77, 286). Respecting the amount of product thus obtained, see page 85 of this volume.

4. *From Starch by the action of Glutin, Malt, or Diastase.* — The product thus obtained is perhaps not dextro-glucose, but maltose (p. 338) — 2 parts of starch well mixed by stirring with 4 pts. of cold water are diffused in 20 pts. of boiling water, and the paste thus formed is digested for eight hours at  $50^\circ$ — $70^\circ$  with 1 pt. of dried and pulverised wheat-

glutin. From the syrup obtained by evaporation, alcohol extracts the sugar, leaving the starch, which is still but slightly altered, and the solution yields the sugar by evaporation.

100 pts. of starch is suspended in 400 pts. of cold water; the mixture is poured into 2,000 pts. of boiling water, and after the whole has cooled to  $65^{\circ}$ , 2 pts. of diastase dissolved in 20 pts. of cold water are added. The mass, which in a few minutes becomes perfectly fluid, is kept for  $2\frac{1}{2}$  hours at a temperature between  $60^{\circ}$  and  $65^{\circ}$ , evaporated as quickly as possible at  $60^{\circ}$ , or better in vacuo, to  $34^{\circ}$  Bm., and left to itself for some days in shallow vessels. By treating the syrup, which is sometimes crystalline, with alcohol of 95 per cent. at a temperature of  $75^{\circ}$ , cooling the solution out of contact of air, filtering, reducing the filtrate to a syrup by distillation and concentration, and leaving the syrup to itself in vacuo, crystals are obtained which may be purified by pressure, renewed treatment with alcohol, and recrystallisation from 4 pts. water at  $65^{\circ}$ , with help of animal charcoal. (Guérin-Varry.) The diastase may be economically replaced by 18 times the quantity of malt. (Guérin-Varry.)

5. *From Linen.* — See page 308. To 12 pts. of linen (purified as completely as possible by treatment first with potash-ley, then with water, and dried: *Vogel*): 17 pts. oil of vitriol are very slowly added, so that no heating may take place; the mass is kneaded together, left to itself for 24 hours, then dissolved in a very large quantity of water; the solution is boiled for 10 hours; the acid is saturated with carbonate of lime; the liquid is filtered and evaporated; and the glucose which separates after some days is purified by recrystallisation. (Braconnot.) *Vogel* uses sulphuric acid of sp. gr. 1.8 (which blackens the linen less than strong oil of vitriol) and leaves the mass to itself for two days.

6. *From the urine of diabetic patients.* — The crystals obtained by evaporating the urine are pressed (after being separated from the chloride-of-sodium compound of glucose) and purified by crystallisation from boiling alcohol (*Chevreul*), or by digestion with cold alcohol and subsequent recrystallisation. (Prout.) Addition of ether to the alcoholic solution favours the crystallisation. (Peligot, Hünefeld.) — The urine is evaporated to a syrup on the water-bath; the residue exhausted with alcohol; the tincture precipitated with basic acetate of lead; the lead separated from the filtrate by sulphuretted hydrogen; and the clear liquid evaporated to a syrup and allowed to stand till it deposits crystals. (Hünefeld, *J. pr. Chem.* 8, 560.) — Frequently nothing but crystals of the chloride-of-sodium compound of glucose are obtained on evaporating diabetic urine. (Lelmann, *Handbuch*, viii, *Zoochem.* 568.)

*Directions for the detection of Sugar in the urine.* — 200 cc. urine are mixed with 800 cc. alcohol, allowed to settle, and then filtered; alcoholic potash is added drop by drop to the perfectly clear liquid, until it has acquired a slightly alkaline reaction; and the mixture is left for 24 hours in the cold. On carefully decanting the liquid and draining it off as completely as possible, the sides of the vessel, when allowed to dry by spontaneous evaporation, are found to be covered with crystalline crusts of the potash-compound of glucose. This is dissolved in a small quantity of water, and the glucose recognised by its browning with potash-ley, by the copper-test, or by its

reaction with basic nitrate of bismuth. (E. Brücke, *Wien. Akad. Ber.* 29, 346; *J. pr. Chem.* 74, 115.)—By precipitating the urine, first with sugar of lead, then with basic acetate of lead, and lastly with ammoniacal acetate of lead, precipitates are obtained, of which the last two contain sugar, although basic acetate of lead does not throw down any sugar from a pure solution of grape-sugar. By pressing each of these two precipitates, dividing them finely, and decomposing them with cold aqueous oxalic acid, filtering, neutralising the filtrate with carbonate of soda, acidulating with acetic acid, concentrating the liquid by evaporation, and precipitating the oxalate of soda by alcohol, a solution is obtained from which glucose can be precipitated as above by alcoholic potash, and recognised in the same way. Carbonate of lime may also be used instead of carbonate of soda. (Brücke, *Wien. Akad. Ber.* 39, 10; *Chem. Centr.* 1860, 231.)

*Estimation of Glucose.*—Barreswil's method (*Arch. d'anatom.* 1846, 50; *J. Pharm.* 6, 361; *Berz. Jahresber.* 25, 556). A known measure of potassio-tartrate of copper mixed with potash-ley is heated to boiling in a capsule, and the liquid containing sugar is dropped in until the copper-solution has become colourless by the separation of red dioxide of copper. The quantity of glucose required to reduce the quantity of copper-solution employed must be ascertained by a preliminary experiment. Barreswil prepares the copper-solution by dissolving 400 grm. carbonate of soda, 500 grm. cream of tartar, 300 grm. sulphate of copper, and 400 grm. hydrate of potash in half a litre of water. — Fehling (*Ann. Pharm.* 72, 106. — 106, 75) adds to a solution of 160 grm. neutral tartrate of potash (or better, 192 grm. tartrate of potash and soda) in a small quantity of water, 600 or 700 cc. soda-ley of sp. gr. 1.12, then a solution of 40 grm. crystallised sulphate of copper in about 160 cc. water, and dilutes the mixture until it measures 1154.4 cc. at 15°. — Five milligrammes (0.005 grm.) of dry glucose can reduce 1 cc. of this solution. It must be kept in well closed vessels, to protect it from carbonic acid and air; the solution ought not to give any precipitate of dioxide of copper when boiled by itself. The sugar-solution to be tested is best employed free from acid. See also Kersting (*Ann. Pharm.* 70, 251), H. Schwarz (*Ann. Pharm.* 70, 54), Roser (*Ann. Pharm.* 74, 180), Donaldson (*J. Chim. méd.* 27, 641; *Lieb. Kopp. Jahresber.* 1851, 647), Mulder (*Lieb. Kopp. Jahresber.* 1850, 614), Neubauer (*N. Br. Arch.* 72, 276), Werther (*J. pr. Chem.* 74, 373), Löwenthal (*J. pr. Chem.* 77, 336), Schiff (*Ann. Pharm.* 104, 330. — 112, 368), Brücke (*Chem. Centr.* 1858, 705. — 1860, 231), Buignet (*N. Ann. Chim. Phys.* 61, 240), and the authorities quoted under milk-sugar (p. 223).

When a solution contains no optically active substance besides glucose, or only cane-sugar in addition, the quantity of dextro-glucose present may be deduced from its rotatory power according to p. 246. Or, as in the case of cane-sugar (p. 243), the quantity of carbonic acid formed by fermentation is determined. On the determination of sugar in diabetic urine by fermentation, see also Wicke (*Ann. Pharm.* 96, 87 and 100); by the optical test, Biot (*Compt. rend.* 15, 633), Lespiau (*Compt. rend.* 26, 305), Robiquet (*Compt. rend.* 43, 920), Listing (*Ann. Pharm.* 96, 93 and 100), also *Handbuch* viii, *Zoochem.* 380; by the depth of coloration produced on boiling the urine with potash-ley, Garrod (*Pharm. J. Trans.* 17, 261).

*Properties.* From alcohol of 95 per cent. (Dubrunfaut, *Compt. rend.* 23, 42), or from stronger alcohol (O. Schmidt), anhydrous dextro-rotatory glucose is deposited in crystals. Microscopic, sharply defined needles,

which melt at  $146^{\circ}$  to a colourless transparent mass. (O. Schmidt.) The crystals frequently contain small quantities of hydrated glucose mixed with them. (Schmidt.) Anhydrous glucose is obtained as a white powder by heating bihydrated glucose to  $55^{\circ}$  or  $60^{\circ}$  in a stream of air; as a melted, transparent, amorphous mass, by heating the bihydrate to  $100^{\circ}$ .—Its taste is less sweet than that of cane-sugar; in the solid state, it is mealy as well as sweet. According to Prout,  $2\frac{1}{2}$  pts. glucose,—according to Dubrunfaut, 2 pts.—glucose sweetens as much as 1 pt. cane-sugar. (See also hydrated glucose, p. 323.)

Molecular rotatory power towards the right, slightly variable between the temperatures of  $18^{\circ}$  and  $80^{\circ}$ , for  $C^{12}H^{12}O^{12}$ ,  $[\alpha]_j = 53.2^{\circ}$  (Dubrunfaut),  $57.44^{\circ}$  (Béchamp),  $55.15^{\circ}$  (Pasteur, according to his determination of the rotation of the chloride-of-sodium compound),  $57.0^{\circ}$  (O. Schmidt),  $56^{\circ}$  (Berthelot): hence for  $C^{12}H^{12}O^{12}, 2H_2O$   $[\alpha]_j = 48^{\circ}$  (Dubrunfaut),  $52.03^{\circ}$  (Béchamp). See also Biot, p. 310. A freshly prepared solution of hydrated glucose (and also of the crystals of anhydrous glucose obtained from absolute alcohol: O. Schmidt), or of dehydrated glucose prepared without fusion, shows a molecular rotatory power equal to twice the above, but it gradually sinks to this point and then remains constant (Dubrunfaut, Pasteur); but if the glucose has been dehydrated by fusion, its solution, even when freshly prepared, possesses the same rotatory power as that acquired, after long standing, by a solution of the crystals (Béchamp, Dubrunfaut). Dubrunfaut distinguishes the glucose contained in a freshly prepared solution as *glucose birotatoire*. The solution of the crystals in wood-spirit retains its greater rotatory power for a longer time than the aqueous solution, so that for  $C^{12}H^{12}(O^{12})^{12}$  there is found  $[\alpha]_j = 106.4^{\circ}$ , or for  $C^{12}H^{12}O^{12}, 2H_2O$   $[\alpha]_j = 96^{\circ}$ ; the rotatory power of the aqueous solution quickly falls, so that the shorter the time that elapses between solution and observation, the nearer is it found to this number. (Dubrunfaut.) The diminution of rotatory power takes place slowly at  $0^{\circ}$  (E. O. Erdmann); it is complete in 24 hours at the common temperature, or in a few minutes at the boiling point. (Dubrunfaut.) It is hastened also by addition of hydrochloric acid. (E. O. Erdmann.)—(Dubrunfaut, *Compt. rend.* 23, 42; *N. Ann. Chim. Phys.* 18, 99.—*Compt. rend.* 42, 228 and 739.—Pasteur, *N. Ann. Chim. Phys.* 31, 95.—E. O. Erdmann, *Lieb. Kopp. Jahresber.* 1855, 671.—Béchamp, *Compt. rend.* 42, 640 and 898.)—The fusion of glucose does not occasion any diminution of its rotatory power, except the disappearance of the bi-rotation. (Ventzke, *J. pr. Chem.* 25, 78.)

	at 100.		Brunner.	O. Schmidt.
			mean.	mean.
12 C.....	72	.... 40.00	..... 39.97	..... 39.56
12 H.....	12	.... 6.67	..... 6.69	..... 6.87
12 O.....	96	.... 53.33	..... 53.34	..... 53.27
<hr/>				
$C^{12}H^{12}O^{12}$ .....	180	.... 100.00	..... 100.00	..... 100.00

Schmidt examined glucose prepared from honey, salicin, and amygdalin, which had been crystallised from alcohol of 97 p. c. The crystals, after being dried in vacuo, lost about 1 p. c. of their weight at  $110^{\circ}$ , owing to the admixture of a small quantity of hydrated glucose. The composition of dextro-rotatory glucose was established by Prout's and Saussure's analyses of hydrated glucose; Liebig (*Ann. Pharm.* 9, 23) deduced the formula from the decomposition of glucose in fermentation. Conflicting views concerning the formula: Brunner (*Ann. Pharm.* 14, 303; 31, 195), Blondeau de Carolles (*J. pr. Chem.* 33, 449).

*Decompositions.* 1. When glucose dried at  $110^{\circ}$  is heated to  $170^{\circ}$ , it gives off 2 at. water, becoming more or less coloured, and is converted into glucosan mixed with a little unaltered glucose and caramel (Gélis, *Compt. rend.* 51, 331). It becomes brown when heated for a long time to  $150^{\circ}$ , and is then hygroscopic after cooling (O. Schmidt). Between  $210^{\circ}$  and  $220^{\circ}$  it swells up more than cane-sugar, gives off a larger quantity of water, and yields caramel (Peligot). The products formed at high temperatures are similar to those obtained from cane-sugar (p. 218), but are somewhat more fusible, more easily soluble in water, and less soluble in alcohol. Alcohol takes up scarcely anything from glucose-caramel; absolute alcohol throws down, from the aqueous solution, a mixture of substances in the form of a black syrup, which becomes moist in the air, and gives precipitates of varying composition with salts of lead or baryta. Caramelin (p. 293) from glucose is also obtained in three states, and is dissolved by long contact with water, even without boiling. (Gélis, *N. Ann. Chim. Phys.* 52, 386.)—By heating glucose in a sealed tube, there is obtained, together with other substances, a liquid which absorbs oxygen and nitrogen from the air with great avidity (P. Thénard, *Compt. rend.* 52, 795).

2. Glucose froths up in the open fire, evolves a smell of burnt sugar, and burns away with flame.—3. Glucose, mixed with spongy platinum, behaves like cane-sugar (p. 251) when heated *oxygen* is passed over it (Reiset & Millon, *N. Ann. Chim. Phys.* 8, 258). Aqueous glucose in contact with platinum-sponge does not absorb oxygen; but, if potash-ley is also added, it becomes heated, and is oxidised to carbonic acid and water (Döbereiner, *J. pr. Chem.* 29, 453).—It yields formic acid when heated with *chromic acid* and sulphuric acid, or with *peroxide of manganese* and sulphuric acid (Hünefeld, *J. pr. Chem.* 7, 44). Aqueous glucose does not alter *bichromate of potash* when heated with it; its presence even prevents the occurrence of the phenomena occasioned by solution of cane-sugar in bichromate of potash (p. 251). (Reich, *J. pr. Chem.* 43, 72.) See also Horsley (*J. pr. Chem.* 63, 320).—By distilling 1 pt. glucose with 1 pt. oil of vitriol, 1 pt. peroxide of manganese, and 30 pts. water, a distillate is obtained which exhibits the reactions of aldehyde, and possesses also the smell of acrolein (Liebig, *Ann. Pharm.* 113, 116).—Glucose is not altered by boiling with peroxide of manganese alone (Stürenberg, *Ann. Pharm.* 29, 291), neither is it altered by *permanganate of potash* (Monier, *Compt. rend.* 46, 425).—It takes fire when triturated with 6 pts. *peroxide of lead* (Böttger). On adding small quantities of glucose to a boiling pulp of peroxide of lead and water, carbonate and formate of lead are obtained.  $C^{12}H^{12}O^{12} + 16PbO^2 = 4C^2H^2PbO^4 + 4PbO,CO^2 + 8PbO + 8H^2O$ . A body which attacks the eyes and nose is formed at the same time (Stürenberg).

4. Glucose behaves like milk-sugar (p. 219) when its *aqueous solution* is heated (Hoppe):—The rotatory power of the aqueous solution does not alter by standing for ten months (Mauméné, *Compt. rend.* 39, 916). A concentrated aqueous solution becomes yellow when heated in a chloride-of-sodium bath, but its rotatory power is hardly altered in 40 to 80 hours (Soubeiran, *N. J. Pharm.* 1, 92).

5. Its aqueous solution mixed with 1 at. bicarbonate of potash and then with 1 at. *iodine*, and warmed, yields iodoform (Millon,



*Compt. rend.* 21, 828; *J. pr. Chem.* 37, 53).—6. Heated in a sealed tube with *bromine* in presence of water, it yields hydrobromic acid, a dark-brown liquid, and humus-like products (Barth & Illasiwetz).—7. *Chlorine* converts glucose into a brown or black mass containing caramelin (p. 262). (Maumené, *Compt. rend.* 30, 314.) *Bichloride of tin* acts upon glucose in the same way as upon cane-sugar (Maumené, *Compt. rend.* 39, 422).

8. Fuming *nitric acid* converts glucose into nitro-glucose (Flores Domonte & Ménard, *Compt. rend.* 24, 89).—When heated with common, or moderately diluted, nitric acid, glucose yields saccharic acid (Heintz) and oxalic acid, but no tartaric acid (Liebig).

9. By heating glucose with syrupy aqueous *phosphoric acid* to  $140^{\circ}$ , a small quantity of a saccharide (p. 317) is obtained (Berthelot, *N. Ann. Chim. Phys.* 54, 81).

10. Glucose dissolves without coloration when triturated with cold *oil of vitriol* (P. Boullay, *J. Pharm.* 16, 172), forming glucoso-sulphuric acid (Peligot, *Ann. Chim. Phys.* 67, 168). It chars when gently heated with 4 pts. oil of vitriol, and evolves carbonic oxide and carbonic acid gases (Filliol, *N. J. Pharm.* 8, 100).—When glucose is boiled with dilute sulphuric acid, the liquid becomes brown and yields a deposit of ulmin and ulmic acid more quickly than when cane-sugar is used (Malaguti), less quickly (Bouchardat); when air has access, formic acid is also produced (Malaguti, *Ann. Chim. Phys.* 54, 417). Coloration occurs quickly with glucose from inverse sugar, more slowly with that from grapes, and in not less than six hours in that from starch (Bouchardat, *J. Pharm.* 21, 627).—11. Glucose long boiled with *hydrochloric acid* becomes unfermentable (Bödeker, *Ann. Pharm.* 117, 111).—12. When heated with aqueous *iodic acid*, it is slowly decomposed into carbonic acid and water (Millon, *N. Ann. Chim. Phys.* 13, 37).—13. Mixed with water and an equal quantity of *arsenic acid*, and exposed to the sun, it becomes red or brown after three or four days (Böttger, *N. Br. Arch.* 17, 185).—14. Honey behaves with *oxalic acid* in the same way as cane-sugar (Döbereiner, *Ann. Pharm.* 2, 338).—15. The rotatory power of aqueous glucose is but very slightly altered by long heating in a chloride-of-sodium bath with *acetic acid* (Soubeiran).

16. By heating dextro-glucose with (organic) acids, compounds are formed, with elimination of water, which belong to the class of *Saccharides*, and possess no longer the properties of the acid and of sugar, but are capable of breaking up again, by assimilating water, into the acid and dextro-glucose (Berthelot).

Berthelot's class of *Saccharides* comprehends all bodies formed in the way above mentioned from the sugars properly so-called. Accordingly, not only dextro-glucose, but lævo-glucose, maltose, and lactose (inosite, eucalin, sorbite) can enter into the composition of saccharides. If they are prepared with cane-sugar or with trehalose, instead of with dextro-glucose, compounds are formed which are either identical with the dextro-glucosides—their formation taking place under circumstances under which cane-sugar is partially, trehalose completely, converted into dextro-glucose—or, at least, behave in the same way so far as they have been hitherto examined.—Berthelot further places in

this class, compounds of starch, dextrin, cellulose, &c., such, for instance, as xyloidin and pyroxilin. He then subdivides the saccharides into —*glucosides*, or those produced from dextro-glucose; *levulosides*, from levo-glucose (levo-rotatory fruit-sugar); *galactosides*, from lactose; and *inosides*, from inosite. [In this work, the first two classes will be spoken of as *dextro-* and *levo-glucosides* whenever it is necessary to distinguish between them.] As to how far the naturally-occurring bitter principles (Laurent's *glucosamides*) ought to be considered as belonging to one of these subdivisions, see below.

The formation of the saccharides occurs for the most part by long contact at 100° or 120°; with some kinds of sugar, as with trehalose, the temperature may be raised as high as 180°. Only a part of the sugar thus enters into combination. — They are decomposable into their constituents under the same conditions as the fats, but with greater difficulty. Water scarcely acts upon them at 100°; at higher temperatures the sugar itself would be destroyed. Continuous boiling with dilute acids decomposes them completely into the original acid and fermentable sugar; part of the latter, however, easily undergoes a further decomposition into glucic acid and humus-like bodies. Some saccharides suffer decomposition by contact with ferments.

The saccharides, like the natural fats, are soluble in water when they contain a volatile acid; insoluble when they contain a fixed acid. The soluble saccharides have an extraordinarily bitter taste; they deflect the plane of polarisation in the same direction as the sugar from which they are derived; none of them are volatile, but in some cases they emit a peculiar smell, which is developed by warming (Berthelot).

The following general account of the saccharides of dextro-glucose, Berthelot's *glucosides*, is taken from Berthelot's *Chimie organique fondée sur la Synthèse* (Paris, 1860), 2, 271. It contains the general formulæ of the saccharides of dextro-glucose, as well as of the similar kinds of sugar, both such as have been actually prepared, and those whose existence must be assumed as probable. The examples are taken from the compounds of milk-sugar, starch, &c., in those cases in which the corresponding compounds of dextro-glucose are unknown.

The saccharides of dextro-glucose are either *mono-*, *bi-*, *ter-*, or *quadri-saccharides*, according as they are derived from 1, 2, 3, or 4 at. dextro-glucose (or, according to Berthelot, from an equal number of atoms of *glucosan*,  $C^{12}H^{10}O^{10}$ , p. 360). Each of these divisions is further divisible into various classes, according as the glucose is combined with 1, 2, or more atoms of acid, and into various sub-classes according as the compounds are formed with elimination of 1, 2, or more double atoms of water.

*S* denotes 1 at. dextro-glucose after separation of 2 at. water, or 1 at. glucosan: in cases where the compound of dextro-glucose is unknown, it stands for 1 at. of a corresponding carbohydrate. — *A* denotes 1 atom of a monobasic acid; *B*, 1 atom of a bibasic acid; and *H*, 1 atom of water.

*Monosaccharides*. —  $\alpha$ . Class I.  $S + A - 2H$ . Formed by the combination of 1 at. glucosan with 1 at. acid, with elimination of 2 at. water. No compounds of this class are as yet known. A corresponding compound of starch is xyloidin, according to Pelouze's formula (p. 107).  $C^{12}H^{10}O^9 \cdot NO^5 = C^{12}H^{10}O^{10} + NO^5 \cdot HO - 2H_2O$ .

$\beta$ . Class II.  $S + 2A - 4H$ . Here belong bistearo-glucose, bi-butyro-glucose and bibenzo-glucose; also glucoso-bitartaric acid (p. 259) formed from the bibasic tartaric acid according to  $S + 2B - 4H$ .

$\gamma$ . Class III.  $S + 3A - 6H$ . Hitherto not prepared. Assuming Strecker's formula for gallo-tannic acid as correct, this body may be taken as an example of a naturally occurring glucoside of this class.  $C^{54}H^{22}O^{34} = C^{12}H^{10}O^{10} + 3C^{14}H^6O^{10}$  (gallic acid)  $- 6H_2O$ .

$\delta$ . Class IV. No saccharides of monobasic acids formed according to  $S + 4A - 8H$  are known, but gluco-tetratartaric acid, formed from bibasic tartaric acid according to  $S + 4B - 8H$ , belongs to this class, and also, among the compounds of (the hypothetical) gallactosan (milk-sugar— $HO = C^{12}H^{10}O^{10}$ ), Berthelot's *acide galactoso-tétratartrique*. Comp. p. 222. (If, with Berthelot, we derive the compounds there spoken of from gallactosan, their formulæ become:—a. *acide galactoso-tétratartrique*,  $C^{44}H^{30}O^{54} = C^{12}H^{10}O^{10} + 4C^8H^6O^{12} - 4H_2O$ ;—b. *acide tri-galactoso-tétratartrique*,  $C^{68}H^{46}O^{70} = 3C^{12}H^{10}O^{10} + 4C^8H^6O^{12} - 8H_2O$ .)

$\epsilon$ . Class V.  $S + 5A - 10H$ . None prepared hitherto.

$\zeta$ . Class VI.  $S + 6A - 12H$ . Sexaceto-glucose,  $C^{36}H^{22}O^{22} = C^{12}H^{10}O^{10} + 6C^4H^4O^4 - 12H_2O$ . Gluco-sexacitric acid, formed from ter-basic citric acid according to  $S + 6B' - 2H$  (thus:  $C^{64}H^{60}O^{92} = C^{12}H^{10}O^{10} + 6C^{12}H^8O^{14} - 2H_2O$ ), also belongs to this place.

The *bisaccharides*, which are similarly divisible into classes, have not hitherto been obtained. The *tersaccharides* of the *first class*, which would be formed according to  $3S + A - 4H$ , are perhaps represented by jalapin [ $C^{68}H^{56}O^{82} = 3C^{12}H^{10}O^{10} + C^{82}H^{30}O^6$  (jalapinic acid)  $- 4H_2O$ ] and by convolvulin [ $C^{62}H^{50}O^{82} = 3C^{12}H^{10}O^{10} + C^{26}H^{24}O^6$  (convolvulinic acid)  $- 4H_2O$ ]. The *fourth class* of tersaccharides is represented by tri-galacto-tetratartaric acid (pp. 222 and 318). Among *quadrisaccharides*,  $4S + B - 2H$ , Berthelot ranks glucoso-sulphuric acid.

17. Gaseous ammonia passed over dextro-glucose which is heated in a water-bath, or to  $110^\circ$ , is energetically absorbed, water holding carbonate of ammonia in solution distilling over, while a brown, tasteless, nitrogenous residue remains. (P. Thénard, *Bull. Soc. Chim. Paris*, 1861, 40; abstr. *Compt. rend.* 52, 444; *Rép. Chim. pure*, 3, 207.)

On pouring upon the residue 20 pts. alcohol of  $38^\circ$ , it separates into an insoluble brown residue and a solution. The former, after being washed with alcohol of  $40^\circ$  and dried in vacuo, contains 52.28 p. c. C., 6.88 H., 9.94 N., and 31.40 O., corresponding, according to Thénard, with the formula  $C^{24}H^{18}N^2O^{21}$  (calculation 51.79 p. c. C., 6.47 H., 10.06 N., and 31.68 O.). It does not evolve ammonia when boiled with potash ley; and when heated with potash-ley and hydrate of baryta to  $120^\circ$ , only as much as corresponds to a small part of the nitrogen it contains, forming at the same time a nitrogenous humous substance. It dissolves in water, aqueous acids and alkalis, gives rapidly alterable precipitates with platinum- and mercury-salts, and reduces ammoniacal copper-salts. (P. Thénard.)

18. Glucose is decomposed by long contact with *alkalis*, *alkaline earths*, and some *metallic oxides*, forming glucic acid. (Peligot.) When glucose is heated with *potash-ley*, the solution becomes dark-brown,

evolves a smell of caramel (Lowitz, Heller), and contains, besides glucic acid, Peligot's melassic acid.

When an alkaline solution of lime in aqueous glucose is allowed to stand for some time, it loses its alkaline reaction and its power of giving a precipitate with carbonic acid. If the lime is removed by means of oxalic acid, a sour unfermentable liquid remains, containing glucic acid together with unaltered sugar. (Peligot.) If air is excluded, lime forms only a small quantity of glucic acid from glucose in 14 days, at the same temperature. (Berzelius, *Jahresber.* 18, 279.) In solutions containing alkaline carbonates, glucose disappears, when exposed to the air, more quickly in proportion as they are more dilute. (Barreswil, *N. J. Pharm.* 17, 121; *J. pr. Chem.* 50, 140.)

Glucose is coloured brown when heated with alkaline carbonates, or with ammonia, in the same way as by potash-ley, but not when heated with alkaline bicarbonates. (Cottureau, *J. chim. méd.* 32, 39.) The alkaline reaction of potash-ley is completely destroyed when it is heated with a sufficient quantity of glucose (Hochstetter, *J. pr. Chem.* 29, 37); when 1 at. glucose is present for each atom of alkali. (Dubrunfaut, *Compt. rend.* 32, 249.) No formic acid is produced in this reaction. (Mathey, *N. Br. Arch.* 72, 289.)

On boiling glucose with baryta-water out of contact with air, a colourless distillate is obtained, which contains acetone. The solution, which is at first wine-yellow, becomes dark brown by ebullition, holds in solution a brown substance, glucate of baryta, and a baryta-salt whence aceto-formic acid ( $C^6H^4O^6, 2H^2O$ ) may be obtained by distillation with sulphuric acid. (Kawaller, *Wien. Akad. Ber.* 30, 159; *J. pr. Chem.* 74, 28; *Chem. Gaz.* 1858, 421.) On adding to glucose, which is kept melted in a water-bath, a hot saturated solution of baryta (or potash- or soda-ley), a violent action takes place, heat is disengaged and steam evolved, while the mass becomes brown, but still however, contains principally glucic acid. If the heat is continued, the mass becomes black, and hydrochloric acid then precipitates from its aqueous solution, black flocks of melassic acid, which dissolve easily in alcohol and contain 61.9 p. c. O., 5.35 H., and 32.75 O. (Peligot.) Peligot's opinion that this acid,  $C^{10}H^{10}O^{10}$  (calculation: 61.54 p. c. C., 4.27 H.), is identical with Svanberg's japonic acid from catechu (*Pogg.* 39, 161) does not accord with the analyses. [Kr.] Besides this, a volatile body is also formed, which easily reduces silver-salts. (Peligot.)

19. A thick syrup of glucose distilled with lime yields an oil, from which metacetone and phorone (xiii, 342) can be obtained by fractional distillation. (Liës-Bodart, *Compt. rend.* 43, 394; *Ann. Pharm.* 100, 354.)

20. Aqueous glucose heated with nitrate of baryta to  $180^\circ$ , for 48 hours, in a sealed tube, yields a body which is insoluble in water and contains a small quantity of nitrogen; while an acid, colourless solution remains, which quickly colours in the air, and contains neither nitric acid nor ammonia, but evolves a large quantity of ammonia when fused at a red heat with hydrate of baryta. (P. Thénard, *Bull. Soc. Chim. Paris*, 1861, 61; *Compt. rend.* 52, 795.)

21. By heating aqueous glucose with aqueous carbonate of soda and basic nitrate of bismuth, a black-brown liquid and grayish-brown precipitate are obtained (Böttger, *Jahrb. pr. Pharm.* 22, 19). Glucose

can be detected in cane-sugar or in urine by means of this reaction (Böttger, *J. pr. Chem.* 70, 432; *N. J. Pharm.* 32, 371).

22. Crystallised glucose, evaporated with excess of *oxide of lead*, loses 11.14 p.c. (10.4 p.c. according to Guérin-Varry) of its weight, but the residue is brown and smells of burnt sugar (Berzelius). A mixture of crystallised glucose with *oxide of lead* loses in weight 28 p. c. at  $110^{\circ}$ , the sugar being converted into melassic acid (Peligot).

23. *Ferric sulphate* and *chloride* are reduced to ferrous salts by boiling with aqueous glucose (Hünefeld, *J. pr. Chem.* 7, 44). — *Ferric hydrate* is reduced in the cold, still more easily on boiling (Kuhlmann, *Compt. rend.* 49, 257). An aqueous mixture of 6 pts. tartaric acid, 240 pts. crystallised carbonate of soda, and 5 or 6 parts crystallised ferric chloride, if heated to boiling, filtered hot, and then mixed with glucose, becomes darker coloured and deposits a precipitate containing ferrous oxide (Löwenthal, *J. pr. Chem.* 73, 71). — 24. A concentrated solution of glucose mixed with *nitrate of cobalt* and a small quantity of fused caustic potash, remains clear on boiling, or, if very concentrated, deposits a light-brown precipitate (Reich). The presence of glucose in a solution of cane-sugar prevents the production of the violet-blue precipitate which solutions of pure cane-sugar give with solutions of cobalt and potash (Reich, *J. pr. Chem.* 43, 72).

25. Honey evolves carbonic acid when brought in contact with freshly precipitated *hydrate of cupric oxide* in the cold, and separates cuprous oxide, whence humus may be extracted by carbonate of soda. The same decomposition takes place more rapidly, but with separation of metal, when the mixture is heated (Busch, *Ann. Pharm.* 4, 57). Glucose behaves like cane-sugar when boiled with cupric hydrate and a small quantity of potash, except that reduction takes place more quickly (Pohl, *J. pr. Chem.* 63, 361). — A concentrated solution of glucose, mixed with an equal quantity of *sulphate of copper*, acquires an emerald-green colour when warmed, and deposits metallic copper, while the supernatant liquid at last becomes brown (Pohl, *J. pr. Chem.* 63, 361). Honey reduces metallic copper from cupric sulphate or *nitrate* when heated, dichloride of copper from *cupric chloride* (Buchner, *Repert.* 2, 1). — An aqueous solution of glucose mixed with *potash-ley* and then with *cupric sulphate*, dissolves the cupric hydrate which separates at first, with a deep blue colour, and deposits cuprous oxide, after some time in the cold, immediately if heated. The production of this precipitate makes it possible to detect and distinguish from cane-sugar, starch, or gum,  $\frac{100}{100,000}$  pt. glucose; by the reddish coloration of the solution,  $\frac{1,000}{1,000,000}$  pt. glucose can be detected (Trommer, *Ann. Pharm.* 39, 361). Comp. Guibourt (*N. J. Pharm.* 13, 263). Carbonic acid is formed during the reduction (also formic acid when the sugar is in excess), together with a peculiar acid, resembling humic acid, which remains in combination with the alkali (Mathey, *N. Br. Arch.* 72, 289). Under the same conditions, 1 at. glucose reduces 5 at. cuprous oxide (formed from 10 at. cupric oxide) from a solution of cupric sulphate mixed with a sufficient quantity of tartaric acid and then with potash,—a solution spoken of in this Handbook as *potassio-tartrate of copper* or *potassio-cupric tartrate* (Comp. p. 313).

Honey, in contact with a saturated solution of verdigris in vinegar, causes, in the cold, an evolution of carbonic acid which begins after

12 hours and lasts for several days, and at the same time (whether in the dark or in sunlight) separation of metallic copper mixed with a little dioxide. Cupric acetate, when boiled with honey, is reduced only to dioxide, which is precipitated, for the most part mixed with humus-like substances. A little dioxide remains dissolved, even when all the acetic acid has been volatilised by long boiling; it must therefore be in combination with a non-volatile acid, probably humic acid, which exists also in the old *oxymel æruginis* (Busch). According to Buchner, honey precipitates cupric acetate only under the influence of light, or on boiling. See also Vogel (*Schw.* 5, 80); Baumann (*N. Br. Arch.* 37, 47).

26. *Mercurous nitrate* is not altered by aqueous glucose at 100° (Baumann).—27. Glucose throws down metallic silver from aqueous *nitrate of silver*, as a black precipitate, on boiling; from aqueous ammonio-nitrate of silver, as a dirty-grey precipitate (Baumann). Ammoniacal glucose throws down silver as a metallic mirror from aqueous silver-salts, in the cold or when heated (Liebig). The metal is also separated when a mixed solution of nitrate of silver and glucose is allowed to stand for 14 days (Schwertfeger, *Jahrb. pr. Pharm.* 7, 292). A solution of glucose, mixed with carbonate of soda, or with potash-ley, reduces chloride of silver to the metallic state on boiling; it reduces carbonate of silver even at 66°—70° (Schiff, *Ann. Pharm.* 109, 68). On heating glucose with oxide of silver and potash-ley, oxalic acid is formed (Liebig, *Ann. Pharm.* 113, 12).—27. Glucose is not changed by ebullition with aqueous *bichloride of platinum* (Baumann).

28. If solution of glucose, mixed with *indigo*, or with solution of indigo, is boiled, and carbonate of soda dropped in, the liquid is decolorised by the conversion of the indigo-blue into indigo-white (E. Mulder, *N. Br. Arch.* 95, 268).

29. An aqueous solution of 1 pt. *red prussiate of potash* mixed with  $\frac{1}{2}$  pt. potash-hydrate, and heated to 60° or 80°, is decolorised when aqueous glucose is dropped in. Inverse sugar behaves in the same way, but cane-sugar and dextrin prepared by roasting (the latter not even after being boiled for a short time with acids) do not decolorise the solution. 100 cc. of a solution containing in that bulk 10.98 grms. red prussiate of potash and 5½ grms. potash-hydrate is decolorised by the inverse-sugar formed from 1 gm. of cane-sugar (Gentile, *Dingl.* 152, 68; *Chem. Centr.* 1859, 504; *Kopp's Jahresber.* 1859, 698). Gentile employs this reaction for the determination of glucose and inverse sugar. *Loc. cit.*; further Stammer's objections (*Dingl.* 158, 40; *Chem. Centr.* 1860, 870), and Gentile's reply (*Dingl.* 158, 427; *Chem. Centr.* 1861, 91). See also p. 308).

30. Dextro-glucose is capable of undergoing *vinous fermentation* (p. 265).—It is not thereby first converted into another kind of sugar, certainly not into levo-glucose; for the liquid has, at every stage of the process, a dextro-rotatory power proportional to the quantity of glucose contained in it, and yields crystals of glucose by evaporation (Ventzke, *J. pr. Chem.* 25, 78; Mitscherlich, *Pogg.* 59, 94; *N. J. Pharm.* 4, 216; Dubrunfaut, *N. Ann. Chim. Phys.* 21, 171).—31. In the *lactous fermentation* (p. 276) of dextro-glucose, the rotatory power diminishes constantly in the proportion corresponding to the quantity of acid formed (Dubrunfaut, *N. Ann. Chim. Phys.* 21, 175).—

*Erythrozym* acts on glucose in the same way as upon sugar (Schunck, *J. pr. Chem.* 63, 222. — See also p. 267).

Left to itself in contact with chalk and cheese (gelatin, or other nitrogenous animal substances) at  $40^{\circ}$ , for weeks or months, an aqueous solution of glucose is capable, according to Berthelot, of undergoing a decomposition, different from fermentation properly so-called which takes place under the influence of yeast, whereby the nitrogenous substance, as well as the sugar, suffers decomposition, and nitrogen, carbonic acid, and hydrogen, are evolved, while alcohol, and butyrate and lactate of lime are formed. Yeast is not produced under these circumstances, unless air has access to the liquid. In other cases, cells resembling yeast make their appearance, without any alcohol being produced; so that, under these particular conditions, yeast and alcohol are independent of each other. The chalk may be replaced by many other carbonates. — 50 grms. glucose, 800 grms. water, 50 grms. chalk and 20 grms. cheese, left to stand at the mean temperature, produced at first lactate of lime, but after 5 months this had disappeared, and the liquid contained butyrate of lime and a quantity of alcohol, amounting to 2 p. c. of the glucose used. Alcohol was also formed after addition of fatty oil, or of oil of turpentine, but there was no lactate of lime; addition of sulphide of carbon prevented the destruction of the sugar. — A mixture of 1 pt. glucose, 10 pts. water,  $\frac{1}{2}$  pt. cheese, and 1 pt. *magnesia alba* contained, after 5 months, alcohol, lactate, and a small quantity of butyrate of lime, the sugar being completely destroyed. In this and in some of the following cases, it remained doubtful whether or not yeast was formed. The same products were formed when an equal quantity of carbonate of baryta was used instead of the magnesia. Alcohol was obtained when the carbonates of zinc, manganese, iron, nickel, and lead, or peroxide of manganese, oxide of zinc, cupric oxide, metallic iron, or metallic zinc were used instead of the magnesia; with oxide of lead and carbonate of copper, no alcohol was obtained. Alkaline carbonates, or borate, phosphate, or hyposulphite of soda, added in equal quantity, did not prevent the production of alcohol. By caustic soda, the sugar was destroyed without yielding alcohol; with sulphite of soda or lime, it remained unaltered. When the magnesia was replaced by carbonate of ammonia, alcohol was formed at the same time as a peculiar acid, the lime-salt of which was deliquescent, and contained at  $110^{\circ}$ , 36.6 p. c. carbon, 5.2 hydrogen, and 18.9 lime, nearly corresponding to the formula  $C^{12}H^{14}CaO^{16}$ . (Berthelot, *N. Ann. Chim. Phys.* 50, 351. — See also p. 279.)

32. If oil of vitriol is gradually added to aqueous solution of ox-gall, until the precipitate at first produced is re-dissolved, the liquid assumes, on addition of a small quantity of solution of glucose, a violet-red colour, similar to that of a solution of permanganate of potash. Cane-sugar and starch also act in the same way. (Pettenkofer, *Ann. Pharm.* 52, 90.) According to Pettenkofer, this reaction is applicable to the detection of sugar in urine, and also in blood, after removal of albumin by boiling with alcohol. — Many other protein-compounds, likewise oil-fat, oil of almonds, and many other oils, behave like gall. (M. S. Schultze, *Ann. Pharm.* 71, 266.) The extractive matter of healthy urine employed in place of sugar, produces the same coloration, which may sometimes be obtained with ox-gall, oil of vitriol and a small quantity of water only. (Van den Broek, *J. pr. Chem.* 39, 362.) ¶. According to Schunck (*Phil. Mag.*

[4], 23, 179) the extractive matters contained in healthy urine yield, when decomposed in aqueous solution by means of strong acids, a sugar possessing the composition and some of the properties of glucose, but uncrystallised and insipid. ¶.

Concerning the supposed formation of fat from sugar by means of bile, see *Handb. buch*, viii, *Zoochem.* 58; Merckel (*Ann. Pharm.* 59, 74; *J. pr. Chem.* 40, 118); Schiel (*Ann. Pharm.* 58, 96); Herzog (*N. Br. Arch.* 47, 149).—On the decomposition of sugar by saliva see *Handbuch*, viii, *Zoochem.* 23; by the intestinal juice, *ibid.* 92; by the pancreatic juice, *ibid.* 89, and during digestion, *ibid.* 580, and elsewhere.

*Combinations. With Water.*—Melted glucose deliquesces at first when exposed to the air by absorption of water (7·9 p. c. : Guérin-Varry) and solidifies, as soon as the quantity of water is sufficient for the formation of crystals, to a crystalline, granular mass. (Gehlen, Mitscherlich). Glucose dried without being melted, absorbs no water when exposed to the air. (Béchamp, *Compt. rend.* 42, 900).—The crystals of anhydrous glucose, obtained from alcohol, if dissolved in a small quantity of water and evaporated over oil of vitriol, are found to have taken up a quantity of water amounting to only 3·1 p. c. of their weight. Anhydrous glucose appears, therefore, capable of existing for some time in aqueous solution. (O. Schmidt). An aqueous solution evaporated to a thin syrup solidifies after a few days to a granular mass; if evaporated to a thick syrup, it does not solidify, owing to the absence of sufficient water, until it has absorbed more water from the air.

a. *Mono-hydrated glucose.* Anthon's *hard-crystallised glucose*—Prepared on the manufacturing scale by a process that is kept secret. In the crystallised state, air-dried, it contains  $C^{12}H^{12}O^{12}, H_2O$ , and does not diminish in weight when placed over oil of vitriol at 13°. (Anthon, *Dingl.* 151, 213; *Chem. Centr.* 1859, 289.)

b. *Bi-hydrated glucose. Crystallised glucose.*—Generally obtained in white, opaque, granular hemispherical or cauliflower-shaped masses, with occasional shining surfaces. The crystals are seen under a magnifying glass to be 6-sided tables, whose lateral faces cut each other at angles of about 120°. They are not, like the similar crystals of lactose, pea-shaped and thicker in the middle, and are not so hard as the latter, but more brittle, and less frequently isolated and well developed. (Pasteur, *Compt. rend.* 42, 349).—Mitscherlich obtained on one occasion transparent well-formed crystals, as much as 0·5 millim. long (bi-hydrated?), which shewed double refraction. (Biot, *Compt. rend.* 23, 909).—Grates between the teeth. Brittle. Sp. gr. 1·3861. (Guérin).

Becomes soft at 60°, softer still at 65°, losing a small quantity of water; at 70° it becomes doughy; at 90°—100° it deliquesces to a thin syrup, and loses in all 9·8 p. c. water. (Guérin-Varry). It melts between 70° and 80°, if dried in vacuo between 90° and 100° (Béchamp), at 86° (O. Schmidt), loses 9 — 9·1 p. c. water (by calculation, 2 at. = 9·09 p. c. water). (Peligot.) In a stream of dry air, it loses only hygroscopic water at 50°, but between 55° and 60°, part of its water of crystallisation, and, if kept at this temperature for a few hours, it may be heated to 80° or 100° without melting. (Béchamp, *Compt. rend.* 42, 898.)



	Crystals.		Saussure. from Grapes.	Prout. from Honey.	Guérin. from Starch.
12 C .....	72	36·86	36·71	36·36	36·30
14 H .....	14	7·07	6·78	7·07	7·20
14 O .....	112	56·57	56·51	56·57	56·50
$C^{12}H^{12}O^{12}, 2HO$ ...	198	100·00	100·00	100·00	100·00

Many other chemists have also analysed bi-hydrated glucose.

c. *Aqueous solution.* — Amorphous melted glucose dissolves in water in all proportions. (Béchamp.) — The concentrated solution has not the elasticity and ropiness of cane-sugar syrup. Crystallised glucose dissolves quickly at first when covered with water, but afterwards more slowly, so that the density of the solution becomes constant only after several days' standing, with frequent shaking. The saturated solution contains 44·96 p. c. anhydrous glucose; its sp. gr. at 15° is 1·206, at 17·5° it is 1·2055. If powdered glucose is shaken with a quantity of water insufficient for complete solution, the sp. gr. of the solution is 1·201 after 36 hours, 1·202 after 50 hours, 1·205 after 74 hours, and 1·206 after 98 hours, and remains constant at this point. Accordingly, at 15°, 1 pt. anhydrous glucose dissolves in 1·224 pts. water, 1 pt. monohydrated glucose in 1·119 pt. water, or 1 pt. bi-hydrated glucose in 1·022 pt. water; but glucose dissolves more freely if it contains foreign substances, and by dissolving hard-crystallised glucose in an equal quantity of (warm) water, a solution of sp. gr. 1·221 at 17·5° is obtained. (Anthon, *Dingl.* 151, 213; *Chem. Centr.* 1859, 289.) The solution of 20 grms. crystallised glucose in  $\frac{1}{10}$  litre water cools the water 4° (Dubrunfaut, *Compt. rend.* 23, 42); 1·2 kilog. dissolved in 2·5 kilogs. water cooled it 6°, and 210 grms. dissolved in 400 grms. water lowered its temperature 5·25°. (Pohl, *Wien. Akad. Ber.* 6, 598.) — The specific gravity of solutions of glucose is about the same as that of solutions of cane-sugar containing equivalent quantities of sugar.

*Table of the quantities of Anhydrous Glucose contained in aqueous solutions of Glucose.* Calculated by Pohl (*Wien. Akad. Ber.* 11, 664) from Graham, Hofmann, & Redwood's determinations:—

Quantity of anhydr. glucose in 100 pts. solution.	Sp. gr. of solution.	Quantity of anhydr. glucose in 100 pts. solution.	Sp. gr. of solution.
2.....	1·0072	15.....	1·0616
5.....	1·0200	17.....	1·0693
7.....	1·0275	20.....	1·0831
10.....	1·0406	22.....	1·0909
12.....	1·0480	25.....	1·1021

*With Salifiable Bases.* — Dextro-glucose forms with the alkalis, alkaline earths, and oxide of lead, compounds which are more easily decomposed than the compounds of cane-sugar. Aqueous glucose takes up a large quantity of baryta, strontia, or lime, and forms yellow solutions, precipitable by alcohol, which, even when protected from the air, become darker, and are decomposed when kept (according to p. 318) or when heated. Their taste is bitter and slightly alkaline, and, when evaporated in vacuo, they leave a transparent, brittle mass, which (sometimes: *Peligo*t) contains unaltered glucose. (Berzelius, *Peligo*t.)

*Potash-compound.* — Dutch syrup shaken for some time with 8 pts.

absolute alcohol, the solution being decolorised by animal charcoal and mixed with alcoholic potash, yields white crystals, which, in absence of free alkali, may be recrystallised from hot alcohol. (Winckler, *Jahrb. pr. Pharm.* 18, 100.) If free alkali is present, the alcoholic solution becomes brown when heated in the air. Winckler likewise obtained this compound from horse-radish sugar. On the preparation of glucosate of potash from urine, see p. 312.

*Soda-compound.* — Obtained like the potash-compound. (Winckler.) — With *borax*, glucose behaves like cane-sugar (p. 284). (Stürenberg, *N. Br. Arch.* 18, 279.)

*Glucose with Chloride of Sodium.* — Dextro-glucose forms two or more compounds with chloride of sodium. (Städeler.) The rotatory power of glucose is not altered by addition of chloride of sodium to its solution. (Pasteur.)

a. *With more than 1 at. Chloride of Sodium.* — By evaporating diabetic urine, saturated with common salt, very small crystals are sometimes obtained, which contain  $1-1\frac{1}{2}$  p. c. water, and more chloride of sodium than the crystals of *b*, corresponding nearly to the formula  $C^{12}H^{12}O^{12}, 2NaCl$ . (Städeler, *Zürcher Mith.* 3, 468; *Pharm. Centr.* 1854, 930.)

b. *With 1 at. Chloride of Sodium.* — Calloud obtained from glucose and common salt, crystals containing 25 p. c. chloride of sodium, the existence of which was afterwards called into question. — The slow evaporation of diabetic urine saturated with common salt furnishes well-formed crystals, but without sufficient lustre to admit of measurement. They contain on an average, 23.01 p. c. chloride of sodium, and lose 3.35 p. c. water at  $130^{\circ}$ . (Städeler.)

	Crystals.			Städeler.
				mean.
12 C .....	72	29.09	.....	28.81
13 H .....	13	5.25	.....	5.30
13 O .....	104	42.02	.....	42.88
NaCl .....	58.5	23.64	.....	23.01
<hr/>				
$C^{12}H^{12}O^{12}, NaCl, HO$ ....	247.5	100.00	.....	100.00

Instead of the crystals of *b*, crystals are sometimes obtained containing between 1 and 2 at. glucose to 1 at. chloride of sodium: probably because the compounds *b* and *c* crystallise together. (Städeler.)

c. *With  $\frac{1}{2}$  at. Chloride of Sodium.* — Discovered by Calloud (*J. Pharm.* 11, 562; *Schw.* 46, 337; *Mag. Pharm.* 11, 257). Crystallises out when diabetic urine is evaporated, also from solutions containing 1 at., or less, of chloride of sodium to 2 at. glucose; according to Brunner, from solutions of glucose saturated with chloride of sodium. When a layer of ether-alcohol is poured upon diabetic-urine syrup, and the whole allowed to stand quietly, transparent crystals of this compound are obtained. (Hünfeld, *J. pr. Chem.* 7, 46.) Glucose from diabetic urine yields this compound far more easily than glucose of different origin. (Erdmann & Lehmann.) Purified by crystallisation from water at the common temperature. (Brunner.)

Transparent, colourless, lustrous crystals, attaining half an inch in length, belonging, according to Pasteur, to the right prismatic or rhombic

system. (Fig. 65.) Rhombic prism  $u$  of  $120^\circ 12'$ , the acute lateral edges being truncated by  $t$ .  $t:u = 119^\circ 54'$ . The summit is formed by the rhombic octahedron,  $\alpha$  and the dome  $i$ ; the rhombohedron  $q$  belongs to an imperfectly developed obtuse rhombic octahedron. In favour of this view (and in opposition to Kobell & Schabus's opinion) is the fact that the crystals are not, as is the case with crystals belonging to the hexagonal system, optically uniaxial, and also that their solution possesses rotatory power. (Pasteur. — See v. Kobell's reply, *J. pr. Chem.* 69, 217). — According to von Kobell & Schabus, the crystals are rhombohedrons belonging to the hexagonal system. Dihexahedric combinations of two rhombohedrons (Fig. 131), the faces  $r$ , and those similarly situated, being but slightly developed; a more obtuse rhombohedron  $q$  forms, by perpendicular truncation of the combination-edge  $r:r_2$  and of the corresponding edges, a three-faced summit imposed on the alternate faces of the dihexahedron; the combination-edge  $r_2:r_4$  and the corresponding edges are truncated by the six-sided prism  $s$  (Fig. 139). Schabus observed also the basal faces  $p$ . Crystals of another habitus showed him the two rhombohedrons (Fig. 131) more equally developed, the horizontal edges being truncated by  $d$ , and the 2- and 2-edged summits truncated by  $s$ .  $r:r_2 = 77^\circ 42'$  (Schabus);  $r:r' = 126^\circ 40'$  (Schabus);  $r':r_4 = 126^\circ 30'$  (Kobell),  $127^\circ 30'$  (Schabus);  $r':q = 161^\circ 30'$  (Kobell.) The crystals examined by Schabus were from diabetic urine and were brown, opaque, and had no perfectly plane faces. (Kobell, *Repert.* 35, 411; *J. pr. Chem.* 28, 489. — Schabus, *Krystalgestalten*, Wien, 1855, 21, erroneously called glucose. — Pasteur, *N. Ann. Chim. Phys.* 31, 95; — *Compt. rend.* 42, 350. — See also Marx, *Schw.* 52, 479; Studer, *Ann. Pharm.* 14, 314.

Molecular rotation to the right  $[\alpha]_D = 47.14^\circ$ , corresponding to the quantity of glucose contained in the compound. In a freshly prepared solution, it exhibits, like glucose, birotation (p. 314) (Pasteur.) — Sp. gr. 1.56—1.58 (Hunt, *Sill. am. J.* [2] 19, 416.) Hardness like that of sugar-candy. Taste sweet and saline.

The crystals contain water and are permanent in the air, but become opaque by standing over oil of vitriol; they then lose gradually, more quickly if powdered, 2 at. water (on an average 4.34 p. c.: *Erdmann & Lehmann*). They lose their water still more quickly in a stream of air at  $100^\circ$ . (*Erdmann & Lehmann*, *Soubeyran*.) This compound loses 6 p. c. water at  $160^\circ$  in vacuo (Peligot), but begins to be decomposed even at  $140^\circ$ ; at  $150^\circ$  it evolves a distinct smell of caramel, and at  $156^\circ$ — $160^\circ$  becomes brown (*Erdmann*, *J. pr. Chem.* 16, 247). — Dissolves easily in water; very difficultly (*Brunner*), easily (*Calloud*), soluble in alcohol. — (Peligot, *Ann. Chim. Phys.* 67, 143. — *Brunner*, *Ann. Pharm.* 31, 195. — *Erdmann & Lehmann*, *J. pr. Chem.* 13, 111. — *Soubeyran*, *N. J. Pharm.* 9, 332).

	Crystals.		Peligot.		Soubeyran.	Erdmann	
			mean.			& Lehmann.	
24 C .....	144	....	32.99	....	32.82		
26 H .....	26	....	5.95	....	5.95	....	5.95
26 O .....	208	....	47.66	....	48.23		
NaCl .....	58.5	....	13.40	....	13.00	....	13.30
2C <sup>12</sup> H <sup>12</sup> O <sup>12</sup> , NaCl + 2HO	436.5	....	100.00	....	100.00		

	Dried.		Erdmann & Lehmann.	Soubeiran. mean.	Brunner.
24 C .....	144	...	34.41	...	34.37
24 H .....	24	...	5.73	...	5.84
24 O .....	192	...	45.88	...	45.85
NaCl .....	58.5	...	13.98	...	13.93
<hr/>					
2C <sup>12</sup> H <sup>12</sup> O <sup>12</sup> ,NaCl	418.5	...	100.00	...	100.00

For Brunner's first analyses, see *Ann. Pharm.* 14, 313; *Pogg.* 31, 319. From them Liebig (*Ann. Pharm.* 14, 317) and Berzelius (*Jahresber.* 16, 211) calculated the above formula. Stiedeler, taking into account the composition of the compound *b*, regards the formula C<sup>12</sup>H<sup>12</sup>O<sup>12</sup>,NaCl,H<sub>2</sub>O + C<sup>12</sup>H<sup>12</sup>O<sup>12</sup>,2H<sub>2</sub>O as more probable. Peligot ascribes to the dry compound the formula C<sup>12</sup>H<sup>12</sup>O<sup>12</sup>,NaCl.

*Baryta-compounds.* — a. *Two-thirds?* A solution of glucose in wood-spirit is mixed with a solution of baryta (not in excess) in aqueous wood-spirit; the precipitate is washed with wood-spirit and dried in vacuo, first over quicklime, then over oil of vitriol. (Peligot.) Soubeiran precipitated a mixture of baryta-water and excess of glucose with alcohol. — Acquires a bright yellow colour at 100° in vacuo, without undergoing further alteration; at a higher temperature, it froths up and chars. (Peligot.)

	According to Peligot.		Peligot. mean.
24 C .....	144	.....	23.02
28 H .....	28	.....	4.48
28 O .....	224	.....	35.81
3 BaO .....	229.5	.....	35.69
<hr/>			
C <sup>12</sup> H <sup>12</sup> O <sup>12</sup> ,3BaO	625.5	.....	100.00

	According to Soubeiran.		Soubeiran. mean.
24 C .....	144	.....	24.41
24 H .....	24	.....	4.07
24 O .....	192	.....	32.54
3 BaO .....	229.5	.....	38.98
<hr/>			
C <sup>12</sup> H <sup>12</sup> O <sup>12</sup> ,3BaO	589.5	.....	100.00

Soubeiran dried his substance for 3 months in vacuo. Peligot found on one occasion 37 p. c. baryta. He appears to have dried his substance at 100°, and to have burned it with oxide of copper, whereby some of the carbonic acid must have remained with the baryta.

b. *1 at. : 1 at.* — Alcoholic hydrate of baryta is added to excess of glucose dissolved in alcohol, the precipitate is washed with strong alcohol, and dried in vacuo over sulphuric acid. — A nearly white, loose powder, of a caustic taste; easily soluble in water. (W. Mayer, *Ann. Pharm.* 83, 138.)

			W. Mayer.
12 C .....	72	.....	29.09
11 H .....	11	.....	4.44
11 O .....	88	.....	35.56
BaO .....	76.5	.....	30.91
<hr/>			
C <sup>12</sup> H <sup>11</sup> O <sup>11</sup> ,BaO	247.5	.....	100.00

Mayer prepared the compound from glucose obtained by the decomposition of con-

volvulin and convolvulic acid, but ordinary glucose gave the same compound and not the compound *a*.

*Lime-compound.* — A freshly prepared solution of hydrate of lime in aqueous glucose is precipitated with alcohol. (Peligot.) Soubeiran agitates glucose with milk of lime, adds a small quantity of glucose to the filtrate to neutralise the excess of lime, and precipitates with alcohol. It does not become perfectly dry till it has stood a long time in vacuo. (Soubeiran.)

<i>In vacuo.</i>				Soubeiran. <i>mean.</i>
12 C .....	72 .....	30.51 .....	30.25	
12 H .....	12 .....	5.09 .....	5.06	
12 O .....	96 .....	40.67 .....	41.24	
2 CaO .....	56 .....	23.73 .....	23.45	
$C^{12}H^{12}O^{12}, 2CaO$ ... 236 .....				100.00

$C^{24}H^{28}O^{28}, 3CaO$ , according to Peligot. Berzelius found 24.26 p. c. lime.

*Lead-compounds.* — Aqueous glucose dissolves oxide of lead (but slightly on boiling: *Guérin-Varry*), forming at the same time, though with difficulty, an insoluble basic compound, which becomes brown and is decomposed even below  $100^{\circ}$ . (Berzelius *Lchrb.* 3 Aufl. 6, 434). Glucose is decomposed when heated with oxide of lead: see above, p. 319. Aqueous glucose gives no precipitate with either neutral or basic acetate of lead; the precipitate caused by ammonia in a solution of sugar of lead, yields, when dissolved in water by heat, no precipitate in an aqueous solution of glucose, but, in an alcoholic solution, a precipitate which is soluble in water. (Payen, *Ann. Chim. Phys.* 65, 241.) — The precipitate produced in aqueous glucose by ammoniacal sugar of lead becomes red when the liquid is left to stand, and still more so when it is warmed. A red precipitate is likewise produced when aqueous glucose is boiled with basic acetate of lead, then heated with alcohol and left to cool. (O. Schmidt.)

a. *Quadrifasic.* — 25 pts. aqueous ammonia is added to the mixed solution of 20 pts. dextro-glucose (or inverse sugar, according to Soubeiran) and 35 pts. neutral acetate of lead in 400 pts. water, and the precipitate is dried, first in vacuo, then at  $100^{\circ}$  (Soubeiran).

				Soubeiran.
12 C .....	72 .....	12.16 .....	11.98	
8 H .....	8 .....	1.35 .....	1.36	
8 O .....	64 .....	10.81 .....		
4 PbO .....	448 .....	75.68 .....	73 to 75	
$C^{12}H^8Pb^4O^{12}$ ... 592 .....				100.00

b. *Terbasic.* Ammoniacal sugar of lead is added to excess of glucose-solution, till the precipitate, which disappears at first, becomes permanent. The white precipitate washed out of contact with carbonic acid, and dried in vacuo, turns yellow at  $150^{\circ}$  without further alteration (Peligot).

				Peligot.	Stein.
12 C.....	72	....	14.20	.... 14.0	..... 14.1
11 H.....	11	....	2.17	.... 2.1	..... 2.1
11 O.....	88	....	17.36	.... 17.7	..... 17.8
3 PbO.....	336	....	66.27	.... 66.2	..... 66.0
<hr/>					
$C^{12}H^{11}O^{21}, 3PbO$	507	....	100.00	.... 100.0	..... 100.0

So according to Stein (*Ann. Pharm.* 30, 84); according to Peligot, it is  $C^{12}H^{11}O^{21}, 6PbO$ . Soubeiran always obtained the compound *a*, whatever process he adopted.

Glucose prevents the precipitation of *sesquichloride of iron* by alkalis and other reagents (Rose).

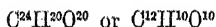
Dextro-glucose is soluble in cold, and still more in hot *alcohol*. Added, in the pulverised state, to alcohol at the temperature of  $17.5^{\circ}$ , 1 pt. (nearly) of anhydrous glucose dissolves in 50.2 pts. alcohol of sp. gr. 0.837, in 9.7 pts. alcohol of 0.880, in 4.6 pts. alcohol of 0.91, in 1.7 pts. alcohol of 0.95. The solution, left to itself for some days, deposits so much of the glucose, that 1 pt. remains dissolved in 50.54 pts., 11.34 pts., 5.25 pts., and 2.07 pts. of alcohol of the specific gravities above-mentioned. — On boiling the alcohol, 1 pt. of anhydrous glucose dissolves in 4.6 pts. alcohol of sp. gr. 0.837, or in 0.73 pt. alcohol of sp. gr. 0.88; on leaving the solution to cool, part of the glucose crystallises out, but the quantity remaining in solution is greater than the same alcohol would have taken up by agitation at lower temperatures, so that after 6 days, 100 pts. of the solution prepared with alcohol of sp. g. 0.837, retains 2.9 pts., and 100 pts. of the solution prepared with alcohol of sp. gr. 0.88 retains 12.4 pts. of anhydrous glucose (Anthon, *Chem. Centr.* 1860, 292).

The crystals which separate by cooling or evaporation are anhydrous, or hydrated according to the strength of the alcohol. They retain alcohol obstinately; so that it is perceptible to the taste even after 16 years (Berzelius, *Lehrb.* 3 Aufl. 6, 434). A similar observation was made by Guérin-Varry. When anhydrous glucose is heated with an equal quantity of alcohol of sp. gr. 0.95, the temperature sinks 5 degrees (Anthon).

From an alcoholic solution of glucose, *ether* precipitates a thick syrup (Döbereiner, *Ann. Pharm.* 14, 249), a crystalline powder (Hünefeld, *J. pr. Chem.* 7, 44).

### Appendix to Dextro-glucose.

#### Glucosan



GÉLIS. *Compt. rend.* 51, 331; abstr. *Zeitsch. Ch. Pharm.* 4, 57.

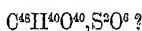
Glucose, dried between  $100^{\circ}$  and  $110^{\circ}$ , gives off water at  $170^{\circ}$ , becoming coloured at the same time, and is converted into glucosan, with which, however, small quantities of caramel and unaltered sugar remain mixed, the latter removable by yeast, the former by charcoal.

Colourless mass, scarcely sweet to the taste. Turns the plane of polarisation to the right, somewhat less strongly than dextro-glucose.

Does not ferment immediately, but only after being treated with dilute acids, which convert it into glucose.

*Conjugated Compounds of Dextro-glucose.*

**Sulphosaccharic Acid.**



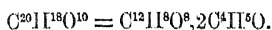
PELIGOT. *Ann. Chim. Phys.* 67, 168.

*Trauben Zucker-schwefelsäure. Acide tétraglucososulphurique* (Berthelot, *Chim. organ.* 2, 280). See page 318. On Sulphamidonic acid see page 104; and on Sulpholignic or Lignosulphuric acid, page 164. — Known only in combination with water or with bases.

1½ pt. oil of vitriol is added, by small portions, to 1 pt. of glucose melted at the heat of the water-bath, the mixture being continually stirred, and the vessel, if necessary, plunged into cold water. If the glucose is impure, or the heat rises too high, the product becomes somewhat brown, which, however, does not affect the purity of the lead-salt. The mixture, diffused in a large quantity of water, is saturated with carbonate of lime; acetate of baryta is added to the filtrate as long as a precipitate of sulphate of baryta is thereby produced, and the liquid again filtered, is precipitated with basic acetate of lead. If the liquid, after precipitation with acetate of baryta, still remains brown, the colouring matter is removed by a small quantity of basic acetate of lead, and the pure salt is precipitated from the filtrate by a larger quantity. The precipitate, washed, and decomposed under water with hydrosulphuric acid, yields *aqueous sulphosaccharic acid*, which tastes at the same time sour and sweet, reddens litmus, decomposes when evaporated in vacuo, and more quickly over the water-bath, into glucose and sulphuric acid, and forms *salts*, almost all of which are soluble.

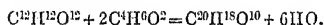
<i>Lead-salt at 170°.</i>				Peligot. <i>mean.</i>
48 C .....	288	...	17.74	18.16
40 H .....	40	...	2.46	2.49
40 O .....	320	...	19.70	
2 SO <sup>3</sup> .....	80	...	4.93	4.50
8 PbO .....	896	...	55.17	53.2 to 55.3
$C^{48}H^{40}O^{40},2SO^3,8PbO$ .....				1624 ... 100.00

# Ethyl-glucose.



BERTHELOT. *N. Ann. Chim. Phys.* 60, 103; *Chim. organ.* 2, 301.

*Glucovinester.* Produced from 1 at. dextro-glucose and 2 at. alcohol, with elimination of 6 at. water:



A mixture of cane-sugar, bromide of ethyl, and hydrate of potash is heated in a sealed tube to 100° for several days, and the product, when cold, is treated with ether; ethyl-glucose is thereby dissolved, and may be obtained by evaporation as a colourless oil. — Has a bitter taste and a faint, agreeable odour. Not volatile.

Berthelot.					
20 C .....	120	...	55.0	.....	54.9
18 H .....	18	...	8.2	.....	7.6
10 O .....	80	...	36.8	.....	37.5
<hr/>					
$C^{20}H^{18}O^{10}$ .....	218	...	100.0	.....	100.0

Resolved by heating with dilute *sulphuric acid* into alcohol and dextro-glucose. — From *potassio-cupric tartrate* it reduces cuprous oxide.

Nearly insoluble in *water*. — From the ethereal solution it is almost completely precipitated by animal charcoal. (Berthelot).

# Hexaceto-glucose.



BERTHELOT. *N. Ann. Chim. Phys.* 60, 98; *Chim. organ.* 2, 275.

*Glucose acétique.* A monosaccharide of the sixth order (p. 317).

Obtained by heating glacial acetic acid with dextro-glucose or cane-sugar to 100° for 50 hours, and purified like *hibutyro-glucose* (p. 332). — Trehalose and starch at 180°, and dextrin at 100°, form with acetic acid compounds similar to or identical with this.

Pale yellow or colourless neutral oil, having a bitter taste and faint odour.

Berthelot.					
<i>mean.</i>					
36 C .....	216	...	52.2	.....	52.15
22 H .....	22	...	5.4	.....	5.35
22 O .....	176	...	42.4	.....	42.50
<hr/>					
$C^{36}H^{22}O^{22}$ .....	414	...	100.0	.....	100.00

Becomes acid in contact with the *air*. — Turns brown when heated,



and burns with an odour of caramel. — Carbonised by *oil of vitriol*; slowly decomposed, by boiling with *dilute sulphuric acid*, into acetic acid and dextro-glucose, which is further partly resolved into humous substances. — With *alcoholic hydrochloric acid*, it forms acetate of ethyl and dextro-glucose. — Hexaceto-glucose reduces *potassio-cupric tartrate*.

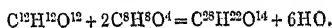
Dissolves abundantly in *water*, but not in all proportions, and is precipitated from the solution by chloride of calcium. — Soluble in *alcohol* and in *ether* (Berthelot).

### Bibutyro-glucose.



BERTHELOT. *N. Ann. Chim. Phys.* 60, 96; *Chim. organ* 2, 290.

*Dibutyrynglucose. Glucose butyrique.* A monosaccharide of the second order (p. 317):



*Formation.* Produced in larger quantity from cane-sugar, dextro-glucose, or trehalose; in small quantity from dextrin, by heating with butyric acid. Traces of the same or a similar compound are obtained when cotton or paper is heated with oil of vitriol and butyric acid.

*Preparation.* Butyric acid is heated with cane-sugar or anhydrous dextro-glucose to  $100^\circ$  for 50 or 60 hours; the mass is exhausted with alcohol; and the solution filtered and evaporated. The residue is mixed with concentrated aqueous carbonate of potash, a lump of caustic potash being added to neutralise it completely, the mixture is shaken up with ether, the ethereal layer is decolorised with animal charcoal, and the filtrate is evaporated over the water-bath.

*Properties.* Pale yellow, viscid oil which produces grease-spots on paper. Neutral, very bitter, with a slightly aromatic odour. Retains water obstinately.

					Berthelot.
					<i>mean.</i>
28 C	.....	168	....	55.6	..... 55.55
22 H	.....	22	....	7.3	..... 7.45
14 O	.....	112	....	37.1	..... 37.00
$C^{28}H^{22}O^{14}$ .....					302 .... 100.0 ..... 100.00

*Decomposition.* 1. Burns when heated, emitting an odour of caramel. — 2. Carbonised by *oil of vitriol*, and resolved, by heating with *dilute sulphuric acid*, into butyric acid and dextro-glucose. — 3. With *alcoholic hydrochloric acid* it yields dextro-glucose and butyrate of ethyl. — 4. From *potassio-cupric tartrate*, it reduces cuprous oxide.

Dissolves sparingly in *water*, easily in *alcohol* and in *ether*. (Berthelot).

### Glucosuccinic Acid.

A mixture of cane-sugar and succinic acid in equal numbers of atoms, heated to between  $120^{\circ}$  and  $130^{\circ}$ , melts to a brown syrup, with elimination of water. The product is an acid compound of glucose with succinic acid, which decomposes at  $100^{\circ}$ , with formation of humus, and forms with lime a salt soluble in water, insoluble in alcohol, See page 259 (Van Bernunelen, *Kopp's Jahresber.* 1858, 436).

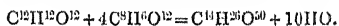
### Glucotetratartaric Acid.



BERTHELOT. *N. Ann. Phys. Chim.* 54, 78; abstr. *Compt. rend.* 45, 268; *N. J. Pharm.* 33, 95; *Chem. Gaz.* 1857, 441; *J. pr. Chem.* 73, 159. — *Chem. organ.* 2, 295.

*Glucotartaric acid*, belongs to the monosaccharides of the fourth order (p. 317). — Different from the *glucobitaric acid* obtained from cane-sugar and tartaric acid (p. 259), which is a monosaccharide of the second order.

*Formation.* By heating dextro-glucose with tartaric acid:



*Occurrence.* Appears to exist in grapes at the time of ripening. When expressed grape-juice is saturated with chalk, filtered, strongly concentrated, filtered again, precipitated with 2 vol. alcohol, and the precipitate purified by washing with weak alcohol, re-solution in water, and re-precipitation with alcohol, a lime-salt is obtained which reduces potassio-cupric tartrate like glucotetratartarate of lime, and is resolved by acids into dextro-glucose and an acid which exhibits the character of tartaric acids.

*Preparation of the Lime-salt.* An intimate mixture of equal parts of dextro-glucose and tartaric acid is heated for a day or two to  $120^{\circ}$  in an open vessel; the cooled mass is triturated with carbonate of lime and a small quantity of water; and the liquid is filtered. Tartrate of lime, with the excess of carbonate, then remains on the filter, while the solution contains the lime-salt of the new acid, together with excess of glucose. On precipitating this solution with twice its volume of alcohol, collecting the precipitate, washing it with dilute alcohol, dissolving in water, again precipitating with alcohol, and repeating the same series of operations a third time, the lime-salt is obtained free from sugar. It is dried for a week or a fortnight in vacuo, then completely by heating it to  $110^{\circ}$ .

*Aqueous glucotetratartaric acid* is obtained by decomposing the lime-salt with excess of oxalic acid.

The aqueous solution of the acid and its salts is gradually resolved, by boiling, into dextro-glucose and tartaric acid, the decomposition

being accelerated by a small quantity of sulphuric acid. — The lime- and magnesia-salts reduce potassio-cupric tartrate. — Not fermentable.

Glucotetratartaric acid is *quadri-basic*. The baryta- magnesia- and lead-salts are obtained like the lime-salt, by using carbonate of baryta, magnesia, or lead, instead of carbonate of lime. The salts still retain water at  $110^{\circ}$ .

*Lime-salt*. — White amorphous powder, 100 pts. of which reduce as much potassio-cupric tartrate as 23 pts. of dextro-glucose (calc. 22.5 pts.) After drying in vacuo, it gives off 14.1 p.c. water at  $110^{\circ}$  (15 at. = 14.4 p.c.).

	at $110^{\circ}$ .		Berthelot.	
44 C .....	264	.... 32.9	..... 33.2	
26 H .....	26	.... 3.3	..... 4.3	
50 O .....	400	.... 49.9	..... 49.8	
4 CaO .....	112	.... 13.9	..... 12.7	
<hr/>				
$C^{44}H^{22}Ca^4O^{50}, 4HO$ ....	802	.... 100.0	..... 100.0	

*Magnesia-salt*. — The salt, dried in vacuo, gives off 26.4 p.c. water at  $110^{\circ}$  (36 at. = 26.38 p.c.).

	at $110^{\circ}$ .		Berthelot.	
44 C .....	264	.... 29.2	..... 30.1	
32 H .....	32	.... 3.5	..... 4.0	
56 O .....	448	.... 49.6	..... 48.9	
8 MgO .....	160	.... 17.7	..... 17.0	
<hr/>				
$C^{44}H^{22}Mg^4O^{50}, 4MgO + 10Aq.$ ....	904	.... 100.0	..... 100.0	

Berthelot's formula contains, by error, 4MgO more, *Chim. organ.* 2, 296, and *N. Ann. Chim. Phys.* 54, 79.

*Lead-salts*. — The acid forms, with lead-oxide, a neutral (quadri-basic) and an acid (bibasic) salt. The former is insoluble, or becomes so during preparation.

*Bibasic*. — Gives off 10.9 p.c. water at  $110^{\circ}$  after drying in vacuo (12 at. = 10.76 p.c.).

	at $110^{\circ}$ .		Berthelot.	
44 C .....	264.0	.... 29.4	..... 29.9	
24 H .....	24.0	.... 2.7	..... 3.6	
48 O .....	384.0	.... 43.0	..... 43.4	
2 PbO .....	223.4	.... 24.9	..... 23.1	
<hr/>				
$C^{44}H^{24}Pb^2O^{50}$ .....	895.4	.... 100.0	..... 100.0	

## Glucohexacitric Acid.



BERTHELOT. *N. Ann. Chim. Phys.* 54, 81.

*Glucocitric acid, Glucosohexacitric acid*. — Belongs to the monosaccharides of the sixth order (p. 317).

When dextro-glucose is heated with citric acid, and the product treated in the manner already described for the tartaric acid compound (p. 333), the lime- (or magnesia-) salt is obtained, which reduces potassio-cupric tartrate, and appears to consist of  $C^{84}H^{40}Ca^{16}O^{32}, 4HO$  (Berthelot).

## Bibenzoyl-glucose.



BERTHELOT. *N. Ann. Chim. Phys.* 60, 98; *Chim. organ.* 2, 293.

*Dibenzoylglucose, Glucose benzoïque or dibenzoïque.* A monosaccharide of the second order (p. 318).

Obtained by heating benzoic acid with dextro-glucose or cane-sugar to  $100^{\circ}$  for 50 hours, and purified like bibutyro-glucose (p. 332). The same (or a similar) compound is produced by heating benzoic acid with trehalose to  $180^{\circ}$ , or with cotton to  $200^{\circ}$ , also, at ordinary temperatures, in a mixture of cotton, oil of vitriol, and benzoic acid; in all cases, however, only in small quantity.

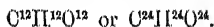
Neutral, semi-fluid oil, which produces grease-spots on paper. Tastes bitter and pungent.

						Berthelot.
40 C .....	240	....	64.8	.....	64.2	
18 H .....	18	....	4.9	.....	5.3	
14 O .....	112	....	30.3	.....	30.5	
<hr/>						
$C^{40}H^{18}O^{14}$ ....	370	....	100.0	.....	100.0	

*Burns* with an odour of caramel when heated. — *Carbonised by oil of vitriol* — With *alcoholic hydrochloric acid*, at a moderate heat, it yields benzoate of ethyl and dextro-glucose. — *Reduces potassio-cupric tartrate.*

Dissolves sparingly in *water*, easily in *alcohol* and in *ether*.

## Lævo-glucose.



BOUCHARDAT. *Compt. rend.* 25, 274.

DUBRUNFAUT. *N. Ann. Chim. Phys.* 21, 169; *J. pr. Chem.* 42, 418; *Pharm. Centr.* 1847, 889. — *Compt. rend.* 29, 51; abstr. *Pharm. Centr.* 1849, 643. — *Compt. rend.* 42, 901; *J. pr. Chem.* 69, 438. — *Compt. rend.* 42, 803; *J. pr. Chem.* 69, 208.

*Linksfruchtzucker.* Occurs in *gum-sugar (Schleimzucker)* or *fruit-sugar* in an impure state, mixed sometimes with dextro-glucose or cane-sugar, sometimes with dextrin or gum. It was recognised as a substance distinct from cane-sugar, even in the last century, and examined by Lowitz (*Crell. Ann.* 1792, 1, 345), Deyeux (*Scher. J.* 3, 528), and

Proust (*N. Gehl.* 2, 77); but no certain mode of discrimination was known, till Biot showed that the different kinds of sugar may be distinguished from one another by their rotatory power. Lævo-glucose was first obtained in the pure state by Dubrunfaut.

Lævo-rotatory *inverse-sugar*, the mixture of lævo- and dextro-glucose in equal numbers of atoms produced by the inversion of cane-sugar (p. 254), was frequently mistaken for dextro-glucose, or regarded as a peculiar sugar convertible into cane-sugar by molecular alteration, till its true nature was pointed out by Dubrunfaut. The following substances, which have been regarded as peculiar sugars, appear to be mixtures resembling inverse-sugar.

a. Mitscherlich's *Caramel*. Obtained by heating cane-sugar with a small quantity of water to a temperature somewhat above  $160^{\circ}$  in the chloride-of-zinc bath. Amorphous, slightly-coloured mass, destitute of rotatory power (Mitscherlich, *Pogg.* 59, 96). According to Gélis (*Compt. rend.* 48, 1062), it is perhaps a mixture of dextro-glucose, levulose (p. 338), and lævo-glucose, produced by the action of water on levulose.

b. Ventzke's *Syrup-sugar*. Obtained by the continued boiling of an aqueous solution of cane-sugar between  $105^{\circ}$  and  $106^{\circ}$ . Colourless syrup, without rotatory power, and not acquiring any by prolonged boiling. Under these circumstances, according to Soubeiran, inverse sugar is produced, which often contains unaltered cane-sugar (Ventzke, *J. pr. Chem.* 25, 75).

c. Soubeiran's *Chylarose*, or *Liquid Sugar from Honey*, having a rotatory power  $[\alpha]_j = -43.51^{\circ}$  at the temperature of  $13^{\circ}$ . Doubtless lævo-glucose, not perfectly freed from dextro-glucose (Soubeiran, *N. J. Pharm.* 16, 252).

d. Michaelis' *Null- and Links-teutlose*. The existence of these sugars is inferred by Michaelis from the rotatory power of certain beet-juices (*J. pr. Chem.* 74, 385; *Chem. Centr.* 1858, 904).

*Occurrence of Lævo-glucose.* — As inverse-sugar in honey, in many fruits and other sacchariferous vegetable organs. (pp. 339 and 305.) The isolated occurrence of lævo-glucose has not been demonstrated with certainty; nevertheless some kinds of apple and pear contain more lævo- than dextro-glucose, perhaps because the mixture of these two substances in equal numbers of atoms first produced by the inversion of cane-sugar, has already suffered an alteration chiefly affecting the dextro-glucose (Buignet, *N. Ann. Chim. Phys.* 61, 264).

*Formation.* 1. In the inversion of cane-sugar (p. 254) by water, dilute acids, yeast, or the peculiar substance of fruits, a mixture of lævo- and dextro-glucose is produced (Dubrunfaut). — 2. By boiling levulose (p. 338) with water or dilute acids (Gélis, *Compt. rend.* 48, 1062). — 3. The sugar produced by continued heating of inulin (p. 115) with dilute acids, is lævo-rotatory (Biot, *Ann. Chim. Phys.* 62, 28; Bouchardat), and identical with lævo-glucose (Dubrunfaut). This substance is likewise produced by continued heating of inulin with water (Dubrunfaut). Unwashed sour yeast also converts inulin into sugar (Bouchardat).

*Preparation.* *From Inverse sugar.* When 10 grms. inverse-sugar are intimately mixed with 6 grms. hydrate of lime and 100 grms. water,

the mass which is liquid at first, solidifies after a certain amount of agitation, and yields, by strong pressure, a solution of the lime-compound of dextro-glucose, while the solid residue, washed and decomposed with oxalic acid, yields lævo-glucose (Dubrunfaut). The inverse sugar occurring in fruits, may be decomposed in like manner (Buignet, *N. Ann. Chim. Phys.* 61, 270).

The inverse sugar occurring in fruits (p. 240), may be obtained, in the absence of other kinds of sugar, by neutralising the juice with chalk, evaporating the filtrate, exhausting the residue with alcohol of 0·85, evaporating the solution, and dehydrating the residue at 110°. (Buignet.)

*Properties.* Colourless, incrystallisable syrup (Dubrunfaut), amorphous solid mass (Bouchardat); after heating to 100°, =  $C^{12}H^{12}O^{12}$ . As sweet as cane sugar. Purgative (Dubrunfaut). Rotatory power varying with the temperature  $[\alpha]_D = -106^\circ$  at 14°C.; =  $-79\cdot5^\circ$  at 52°C.; =  $-53^\circ$  at 90°C. (Dubrunfaut). The lævo-rotary power of inulin-sugar was found by Bouchardat to be at least three times as great as that of inverse-sugar, and likewise variable according to the temperature. Dubrunfaut remarked that when inulin ( $C^{36}H^{60}O^{36}$ , 3110) is boiled with acids, the rotatory power increases to  $\frac{2}{3}$  of its original amount, whence the calculated value of  $[\alpha]_D$  for inulin-sugar is  $-101^\circ$ , and for inulin,  $-38\cdot43^\circ$ .

The supposition that lævo-glucose may be converted into dextro-glucose by boiling with acids or by molecular alteration, has been refuted by Dubrunfaut.

The rotatory power of *inverse sugar* likewise varies with the temperature as well as that of lævo-glucose, as observed by Mitscherlich (*Pogg.* 59, 94) and Ventzke (*J. pr. Chem.* 28, 101) in inverse sugar and in honey. The molecular rotatory power of inverse sugar amounts, for  $C^{12}H^{12}O^{12}$ , to  $[\alpha]_D = -28^\circ$  at 14°C.; at 52° it is only half as great, at 86° it disappears altogether, and at still higher temperatures the inverse sugar becomes dextro-rotatory (Dubrunfaut). The molecular rotatory power, which for  $C^{12}H^{12}O^{12}$  at 15°C is  $[\alpha]_D = -26^\circ$  decreases by 0·37° for each degree above 15° and increases by the same amount for each degree below (Buignet, *N. Ann. Chim. Phys.* 61, 238). Inverse sugar heated in the water-bath contains, on the average, 39·97 p. c. C., 6·67 H., and 53·36 O., corresponding to the formula  $C^{12}H^{12}O^{12}$  (Soubeiran, *N. J. Pharm.* 9, 357; Mitscherlich).

*Decompositions.* Lævo-glucose when heated yields a product analogous to the glucosan (p. 329) of dextro-glucose, but more easily decomposable (Gélis, *Compt. rend.* 51, 331; *Zeitschr. Ch. Pharm.* 4, 57). Probably therefore lævolusan (Kr.). — Lævo-glucose in contact with yeast undergoes vinous fermentation, without previous conversion into another kind of sugar. (Dubrunfaut). — The other reactions of lævo-glucose have been studied only with fruit-sugar containing dextro-glucose: they agree with those of dextro-glucose. On the behaviour of inverse sugar when heated with water, see page 253; with acids (p. 254); in vinous fermentation (p. 274); in lactic fermentation (p. 279); and other places. — ¶. When *sodium-amalgam* is added to an aqueous solution of cane-sugar, inverted by the action of dilute sulphuric acid, the excess of acid having been removed, evolution of hydrogen entirely ceases as soon as the liquid has become slightly alkaline, heat is evolved, and, when the action is complete, the solution is found to contain mannite. (Linnemann, *Ann. Pharm.* 123, 136. — See Mannite.) ¶.

*Combination.* With Lime. — Lævo-glucose forms with lime a soluble basic compound, analogous to that of dextro-glucose, which absorbs

oxygen from the air and decomposes. — A second compound, containing 3 at. lime to 1 at. lævo-glucose, forms sparingly soluble microscopic needles, and is decomposed by water when exposed to light and air, the whole deliquescing and the sugar undergoing decomposition (Dubrunfaut).

On the behaviour of inverse sugar to lead-oxide, see page 289. The compounds of fruit-sugar obtained by Soubeiran (*N. J. Pharm.* 9, 329) were obtained with inverse sugar or honey, and doubtless belong to dextro-glucose. (Kr.)

Lævo-glucose is more soluble in *alcohol* than dextro-glucose.

### *Appendix to Lævo-glucose.*

#### Lævolusan.



GÉLIS. *Compt. rend.* 48, 1062; *Chem. Centr.* 1859, 712; *N. Ann. Chim. Phys.* 57, 234; *Kopp's Jahresber.* 1859, 547.

#### *Saccharide.*

See page 247. Cane-sugar quickly heated to  $160^{\circ}$ , and kept in the melted state at that temperature for a moderate time, is converted into a mixture of equal numbers of atoms of lævolusan and dextro-glucose, the latter of which may be removed by fermentation. The remaining liquid (which has a dextro-rotatory power  $[\alpha]_D = 15^{\circ}$  for  $C^{12}H^{10}O^{10}$ ) leaves, when evaporated, a syrup, which does not crystallise even when kept for years, but contains lævolusan partly unaltered, partly metamorphosed.

Lævolusan is converted by *boiling water* and by dilute *acids*, into a fermentable lævo-rotatory sugar, which reduces copper-solution and is probably identical with lævo-glucose.

#### Maltose.

BIOT. *Compt. rend.* 15, 710; 42, 351.

DUBRUNFAUT. *N. Ann. Chim. Phys.* 21, 178; *J. pr. Chem.* 42, 441; abstr. *Lieb. Kopp. Jahresber.* 1847, 793.

The sugar produced from starch-paste by the action of malt (or diastase p. 90) is, according to Dubrunfaut, different from dextro-glucose. It is the first fermentable product formed from starch-paste by the action of acids, or the last formed by the action of gluten or by spontaneous decomposition (p. 91) (Dubrunfaut); Guérin-Varry (*Ann. Chim. Phys.* 60, 32) (who however did not determine its rotatory power), could not perceive that the sugar formed with diastase differed in any respect from dextro-glucose.

The molecular rotatory power of a sugar prepared by Jacquelin, by heating starch in a Papin's digester with  $\frac{1}{800}$  oxalic acid, was found by Biot to be  $[\alpha]_D = 100.6^{\circ}$ . According to Dubrunfaut, this sugar was a mixture of maltose and dextro-glucose. The sugar from a false manna mentioned on page 305 might also, according to Biot, be referred to this head.

Maltose is prepared from starch-paste by the action of malt (somewhat in the manner described at page 311), and purified with alcohol. — Forms crystals similar to those of dextro-glucose, but with a molecular rotatory power three times as great, and not stronger in a recently prepared solution than after the lapse of several hours. Hence it does not exhibit the bi-rotation of dextro-glucose mentioned at page 314. — It expands in crystallising. — It is converted into dextro-glucose by boiling with dilute *sulphuric acid*. — By aqueous alkalis it is not quite so easily altered as dextro-glucose. — By *fermentation* it yields as much alcohol as dextro-glucose, without previous conversion into that substance. When a mixture of dextro-glucose and maltose is fermented, both kinds of sugar are decomposed simultaneously, not one before the other. — Maltose is somewhat less soluble in *alcohol* than dextro-glucose (Comp. Saussure's observations, p. 308). (Dubrunfaut.)

### Mannitose.



GORUP-BESANEZ. *Ann. Pharm.* 118, 273.

When mannite is oxidised under the influence of platinum-black, carbonic acid, formic acid, mannitic acid, ( $C^{12}H^{12}O^{14}$  vid. inf.) an unfermentable substance and a fermentable sugar (mannitose) are produced. The last of these substances, which has not been obtained in the separate state is distinguished from dextro-glucose by the fact that it does not exhibit any molecular rotatory power, even in concentrated aqueous solution.

In the preparation of mannitic acid by leaving a moist mixture of 1 pt. mannite and 2 pts. platinum-black in contact with the air at a temperature between  $30^{\circ}$  and  $40^{\circ}$ , and lixiviating the resulting acid mass with water, a solution is formed containing mannitic acid, the unfermentable substance, and mannitose; and on precipitating the mannitic acid with basic acetate of lead, and treating the filtrate with hydrosulphuric acid, the unfermentable substance and the mannitose remain in the filtered liquid, and are obtained by evaporation as a mixture, which, however, is difficult to free from acetic acid; hence, to prepare the latter substance, it is better to heat the aqueous solution of the acid mass with carbonate of lime, filter when the neutralisation is complete, and precipitate with alcohol. The liquid filtered from precipitated mannitate of lime, if concentrated to a certain extent, further precipitated with alcohol, and then completely evaporated, leaves a yellow syrup which cannot be made to crystallise, even after decoloration with animal charcoal, but if evaporated in *vacuo*, and finally at  $100^{\circ}$ , appears as an amorphous gum.

This gum may be regarded as a mixture of about one-third mannitose and two-thirds of an unfermentable substance perhaps identical with mannitan. The gum contains 43.06 p. c. carbon, 6.92 hydrogen, and 50.02 oxygen, corresponding perhaps to the formula  $C^{12}H^{12}O^{12}, 2C^{12}H^{12}O^{10}$  (calc. 42.52 C., 7.08 H., 50.40 O.). It does not produce the least deflection of the plane of polarisation, even in concentrated solution; it exhibits with *alkalis*, with *cupric oxide* and *potash*, with *basic nitrate* of



bismuth, carbonate of soda, and other reagents, the same behaviour as dextro-glucose, but is not capable of uniting with *chloride of sodium*. Its alcoholic solution mixed with alcoholic *potash* forms a semi-fluid yellow precipitate containing 11.27 p. c. potash, corresponding to the formula  $2C^{12}H^{12}O^{12}.KO$ . — The quantity of carbonic acid evolved in the vinous fermentation of this gum—which is easily set up—as well as the amount of potassio-cupric tartrate which it is capable of reducing, shows that it must contain a quantity of mannitose, equivalent to 32.56 p. c. dextro-glucose. If the mannitose be decomposed by fermentation, the unfermentable substance remains, on evaporation, as a yellow-brown neutral varnish having a faint taste, soluble in water and in alcohol, insoluble in ether, and emitting an odour of caramel when burned. (Gorup-Besancz).

### *Appendix to Dextro-glucose and the Allied Sugars.*

#### General View of the Glucosides.

*Saccharides* (Berthelot), (*Saccharogens*, p. 309)—They occur both in the vegetable and in the animal kingdom.

*Formation.* None of the naturally occurring glucosides have been prepared artificially; but Berthelot has obtained compounds analogous to the glucosides (see *Saccharides*, p. 316), and Hlasiwetz has obtained from phloretic acid and phloroglucin a product corresponding to phloretin, but containing the proximate constituents in different proportions.

Laurent's views on the composition of glucosides, see *Compt. rend.* 31, 353; 35, 163; *N. Ann. Chim. Phys.* 36, 330; for Delffs' formulæ, see *N. Jahrb. Pharm.* 11, 356; Walz's *N. Jahrb. Pharm.* 11, 358.

*Decompositions.* The resolution of glucosides into glucose, or a corresponding product, and a second body, takes place for the most part on boiling with dilute *mineral acids*. Or it is produced by heating the glucoside with aqueous *alkalis* or *baryta-water*. In this latter case, according to Rochleder (*Wien. Akad. Ber.* 24, 32), crystallisable sugar is sometimes obtained, whereas the decomposition with acids yields only uncrystallisable sugar.—Or the separation is effected at mean temperature, and in presence of water, by nitrogenous substances occurring either in the same plants as the glucosides, or in others. Emulsin decomposes amygdalin and many other glucosides; myrosin decomposes myronic acid; erythrozym decomposes rubian.—Some glucosides are likewise decomposed by yeast and by saliva. The products of the decomposition are often further altered by the action of the air or of the acid employed.

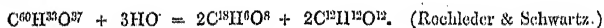
For the *separation* of the decomposition-products from the glucosides, Rochleder (*Wien. Akad. Ber.* 24, 34) gives the following method. The substance, contained in a flask, is treated with dilute hydrochloric acid; the flask is connected, on the one side with a carbonic acid apparatus, on the other with a Liebig's condensing tube. The air contained in the flask is displaced by carbonic acid, and the flask is heated in the water-bath, or, if necessary, in a chloride of calcium

bath. As soon as the decomposition is complete, the contents of the flask are left to cool in a stream of carbonic acid; any product that may have separated out is collected; and the filtrate containing the sugar, hydrochloric acid, and sometimes other soluble products of the decomposition, is mixed with pure carbonate of lead, the addition of which is continued as long as effervescence ensues, after which it is warmed and white lead (prepared by precipitating basic acetate of lead with carbonic acid gas, and washing) is added, whereby basic chloride of lead is precipitated. The precipitate is collected on a filter and carefully washed; moist phosphate of silver is added to the filtrate as long as any reaction ensues between this salt and the dissolved chloride of lead, and till the yellow colour of the phosphate of silver remains visible. The liquid is then filtered; any silver that may be dissolved in the filtrate is precipitated with a very small quantity of white lead; the liquid is heated till the white colour of the precipitate passes into cream-colour, then cooled, filtered, treated with hydrosulphuric acid, and filtered again, and the filtrate is evaporated. Colourless sugar then remains, in case such sugar was formed by the decomposition of the glucosides, whilst the second decomposition-product, even if originally soluble in water, is generally rendered insoluble by the white lead.

The distilled liquid obtained by heating a glucoside with hydrochloric acid, contains, together with hydrochloric acid, any volatile product that may have been formed in the decomposition. It is neutralised with baryta or carbonate of baryta, heated to decompose acid carbonate of baryta, concentrated by evaporation, the greater part of the chloride of barium removed by crystallisation, the rest by sulphate of silver, and the filtrate further examined.

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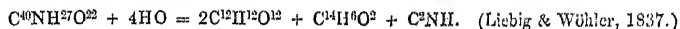
*Aesculin* is resolved, by heating with dilute acids, into *aesculetin* and sugar:



Zwenger and Delffs give other formulae.

The sugar forms crystals, which melt at  $100^\circ$ , are sweeter than grape-sugar, and, like that substance, reduce potassio-cupric tartrate. According to earlier analyses by Rochleder & Schwartz (*Wien. Akad. Ber.* 10, 76), it contains, at  $100^\circ$ , 37.71 p.c. carbon, 6.92 hydrogen, and 55.37 oxygen, corresponding to the formula  $\text{C}^{12}\text{H}^{12}\text{O}^{12}, \text{HO}$ ; according to their more recent analyses (*Wien. Akad. Ber.* 11, 334), it contains, at  $100^\circ$ , 40.50 p.c. C., 7.38 H., and 52.12 O., agreeing with the formula  $\text{C}^{12}\text{H}^{12}\text{O}^{12}$ . It is fermentable.

*Amygdalin*, in contact with emulsin and water, is resolved into sugar, bitter-almond oil, and hydrocyanic acid:

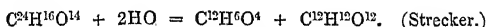


The sugar thus produced is identical in every respect with dextro-glucose (O. Schmidt).

*Apün*, boiled with dilute acids, is decomposed, with separation of flocks. The filtrate, freed from acid, leaves, on evaporation, a sweetish

syrup, which, when boiled with potassio-cupric tartrate, deposits cuprous oxide, but does not give off the odour of caramel when burnt, does not ferment in contact with yeast, cannot be made to crystallise, and dissolves but partially in alcohol, with separation of yellow flocks. Von Planta & Wallace cannot see in these results any evidence of decomposition, and therefore do not regard apiin as a glucoside.

*Arbutin* ( $C^{24}H^{16}O^{14}$ ), boiled with dilute acids, or in contact with emulsin, is resolved into hydrokinone (Kawalier's arctuvín) and grape-sugar (Kawalier):



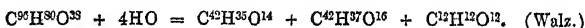
The sugar forms crystals which exhibit the properties of grape-sugar, and when dried at  $100^\circ$  or in vacuo, contain 36.64 p. c. carb., 7.05 hyd., and 56.31 ox., corresponding to the formula  $C^{12}H^{14}O^{14}$  (Kawalier, *Wien. Akad. Ber.* 9, 293).

*Arnícín* ( $C^{70}H^{54}O^{14}$ , or  $C^{48}H^{36}O^{10}$ ) is decomposed by heating with dilute acids, with separation of dark flocks and formation of a substance which reduces cupric oxide (Walz).

*Benzohelícín* is resolved by boiling with dilute acids or aqueous alkalis (not by emulsin), into benzoic acid, salicylic acid, and grape-sugar:

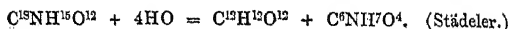


*Bryonín* is resolved, by boiling with dilute acids, into bryoretin, hydrobryotin, and sugar:



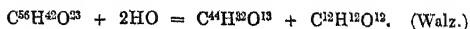
*Cañcín* ( $C^{32}H^{26}O^{14}$ ) is resolved, in like manner, into chiococcaic acid and sugar (Rochleder & Hlasiwetz).

*Chítín*, boiled for 12 hours, or longer, with a mixture of 1 vol. oil of vitriol and 4 vol. water, is resolved, with evolution of ammonia, into amorphous sugar and a second body not yet isolated. Perhaps in this manner:

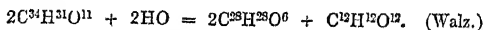


The sugar is fermentable, and reduces cupric tartrate (Berthelot, *Compt. rend.* 47, 230).

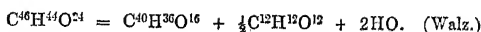
*Colocynthín* is resolved, by boiling with dilute acids, into colocyntheín and sugar:



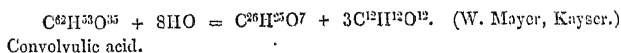
*Convallarín* is decomposed in like manner into convallaretin and sugar:



*Convallamarín* yields under the same circumstances, convallamaretin and sugar:



*Convolvulin* and *Convolvulic acid* are resolved, by oil of vitriol or alcoholic hydrochloric acid, the former with assumption of 5 at., the latter, of 2 at. water, into convolvulinol and sugar:



*Convolvulin-sugar*. — When Kayser (*Ann. Pharm.* 51, 98) decomposed convolvulin by passing hydrochloric acid gas into the alcoholic solution, and, after leaving the mixture to itself for 10 days, extracted the resulting convolvulinol with ether, there remained an acid liquid, which was neutralised with carbonate of lead, filtered and evaporated. From the residue, absolute alcohol extracted a sticky translucent sweetish mass, which reduced cupric oxide, yielded crystals when brought into contact with common salt, fermented with yeast, and exhaled the odour of sugar when burnt on platinum-foil. — Mayer, after decomposing convolvulic acid with dilute sulphuric acid, and removing the convolvulinol, saturated the liquid with carbonate of lead, treated the filtrate with sulphuretted hydrogen, evaporated it to  $\frac{1}{10}$ , removed the separated convolvulin by agitation with ether, evaporated further, and thus obtained a brown sweetish syrup, which behaved like grape-sugar, when burnt, also with an alkaline cupric solution, with bile, with sulphuric acid, with water, and with alcohol whether aqueous or absolute, but did not form a crystalline compound with common salt, and could not itself be made to crystallise. This syrup mixed in alcoholic solution with an alcoholic solution of baryta not in excess, formed a precipitate composed like monoglucosate of baryta (p. 328). (Mayer, *Ann. Pharm.* 83, 138).

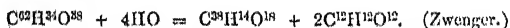
*Crocin* is resolved by dilute acids into crocetin and crocin-sugar :



*Crocin-sugar*, obtained by decomposing crocin in the manner described above, is easily crystallisable, sweet, and reduces from potassio-cupric tartrate, half as much cuprous oxide as dextro-glucose (Rochleder & L. Mayer, *Wien. Akad. Ber.* 29, 6).

*Cyclamin* solidifies when heated with aqueous hydrochloric acid, with formation of sugar and separation of a second product. (De Luca.)

*Daphnin* is resolved by boiling with dilute acids, into daphnetin and sugar :

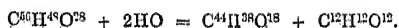


*Datiscin*, treated in the same manner, yields datiscetin and sugar :



The sugar is obtained by evaporation, after removal of the datiscetin and the sulphuric acid, as a sweet syrup, which solidifies in the semi-crystalline form after standing for some time, and reduces potassio-cupric tartrate at 100° (Stenhouse, *Ann. Pharm.* 98, 171).

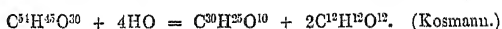
Walz's *Digitalin* is resolved by boiling with dilute sulphuric acid, into digitaliretin, paradigitaletin and sugar. Walz supposes the reaction to consist of two stages: *a*. Resolution of digitalin into digitaletin and sugar :



*b*. Further decomposition of the digitaletin, partly, with abstraction of 4 at. HO, into paradigitaletin, partly into digitaliretin and sugar :

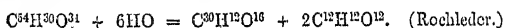


Walz's digitaletin decomposed by dilute acids yields the products above mentioned (Walz, Delffs). Kosmann's *digitalin* and *digitalic acid*, which differ from Walz's compound in composition and properties, are resolved by dilute acids into digitaliretin (which however is not the same as Walz's) and sugar. Decomposition of digitalin :



*Euxanthic acid* ( $C^{42}H^{18}O^{22}$ : Erdmann) is, according to W. Schmid (*Ann. Pharm.* 93, 88) a glucoside, which is decomposed by oil of vitriol into euxanthone and sugar. According to Erdmann, the products formed in this reaction are euxanthone and hamathionic acid (lead-salt =  $C^{14}H^6O^{12}, SO_3, 3PhO$ ); on the other hand, euxanthic acid decomposed by heat yields euxanthone  $C^{40}H^{12}O^{12}$ , carbonic acid and water. The latter decomposition, as well as the formulæ of euxanthic acid and euxanthone, is inconsistent with Schmid's supposition; nevertheless Erdmann's hamathionic acid bears some resemblance to sulphamidonic acid and other compounds of like nature. (Kr.)

*Fraxin* heated with acids yields fraxetin and crystallisable sugar :



*Gallo-tannin* is resolved by boiling with acids into gallic acid and glucose :



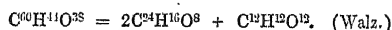
For observations of contrary tendency see gallo-tannin. — The sugar exhibits the reactions and composition of dextro-glucose. (Strecker, *Ann. Pharm.* 90, 331.)

By heating 50 grm. gallotannin with 50 grm. oil of vitriol and 450 grm. water to  $90^\circ$  for three days, and filtering off the gallic acid, a black saccharine solution is obtained, which when neutralised with carbonate of lead, mixed with a slight excess of neutral acetate of lead, concentrated, freed from lead by sulphuretted hydrogen and decolorised by animal charcoal, agrees perfectly with grape-sugar in rotatory power, fermentation and reaction with potassio-cupric tartrate. (Buignet, *N. Ann. Chim. Phys.* 61, 287.)

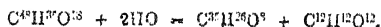
The iodine-compound of a tannin occurring in sweet fruits is likewise decomposed, with formation of dextro-glucose, by boiling with dilute sulphuric acid. (Buignet.)

*Gelatin*. — When isinglass is boiled for some days with dilute sulphuric acid, sulphate of ammonia is formed together with a fermentable sugar. (Gerhardt, *Traité* 4, 509). Hyaline cartilage and rib-cartilage, boiled with hydrochloric acid, yield large quantities of glucose (Fischer & Bodeker, *Ann. Pharm.* 117, 111).

*Globularin*, boiled with dilute sulphuric acid, yields globularetin (part of which changes into paraglobularetin  $C^{24}H^{14}O^6$  [p. 39]) and sugar :

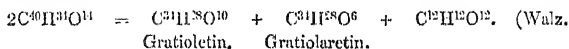


*Glycyrrhizin* is resolved, when its aqueous solution is boiled with hydrochloric acid, into glycyrretin and glucose. Perhaps in this manner.

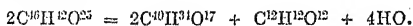


The uncrystallisable sugar exhibits the characters of grape-sugar (Gorup-Besancz). Rotatory power not determined.

*Gratiolin* is resolved, by boiling with dilute sulphuric acid, into gratioletin, gratiolaretin and sugar:



*Gratiosolin* in contact with aqueous acids or alkalis is resolved into gratiosoletin and sugar:



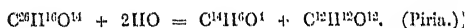
The *gratiosoletin* thus formed is further resolved by boiling into hydro-gratiosolaretin and sugar:



Part of the hydrogratiosolaretin is further converted, with elimination of 2 at. water, into gratiosolaretin,  $C^{31}H^{26}O^9$ . (Walz.)

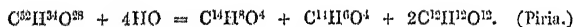
*Helianthic acid*. This name is applied by Ludwig & Kromayer (*N. Br. Arch.* 99, 1, and 285) to a substance, obtained from the seed of the sunflower (*Helianthus annuus*), which is insoluble in cold water and in alcohol, not fermentable, and reduces potassio-cupric tartrate only after boiling with acids.

*Helicin* heated with acids or alkalis, or in contact with emulsin or yeast, is resolved into salicylous acid (xii, 235) and dextro-glucose:



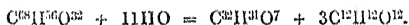
The complete identity of this sugar with dextro-glucose is shown by Schmidt's experiments on salicin-sugar. — *Chlorhelicin* ( $C^{26}H^{16}O^{14}$ ) exhibits a similar reaction, yielding, however, chloro-salicylous (xii, 294) instead of salicylous acid. (Piria.)

*Helicoëidin* is resolved by emulsin into saligenin, salicylous acid and glucose:



*Indican* is resolved by acids or alkalis, *indicamin* by acids, into indiclucin (p. 302) and other products. (Schunck.) See *Indican*.

*Jalappin* in contact with dilute mineral acids is resolved in jalappinol and sugar:



*Jalappic acid*, which contains 3 at. water more, is decomposed in like manner, with assumption of 8 at. water. (W. Mayer.)

*Kinovin* is resolved by alcoholic hydrochloric acid into kinovic acid and kinovin-sugar:



*Kinovin-sugar* is obtained from the alcohol containing hydrochloric acid after separation of the kinovic acid, either by Rochleder's method (p. 340), or as follows: The liquid is neutralised with anhydrous carbonate of soda (or carbonate of lead), and filtered; the precipitate washed with a small quantity of strong alcohol; the alcohol distilled off; and the remaining liquid evaporated to dryness over the

water-bath. The thick residue is dissolved in water, the solution, filtered from the undissolved portion, is evaporated, and the residue is digested in absolute alcohol. The alcoholic solution, when evaporated leaves the kinovin-sugar, to be purified, if necessary, by re-solution and decoloration with animal charcoal. — Amorphous, solid, deliquescent mass, having a faint, somewhat bitter taste. Gives off water when continuously heated over the water-bath. Dried at  $100^{\circ}$ , it contains 43.34 p. c. carbon, 7.72 hydrogen, and 48.94 oxygen, answering to the formula  $C^{12}H^{12}O^{10}$ . It is isomeric or identical with mannitan. Smells like caramel when heated. Reduces potassio-cupric tartrate only in concentrated solution. Dissolves completely in alcohol. (Hlasiwetz, *Ann. Pharm.* 111, 118.)

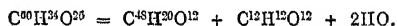
*Kinovatannic acid* is resolved, by boiling with dilute sulphuric acid, into kinova-red, and a substance which behaves with cupric sulphate and potash-ley like grape-sugar. (Hlasiwetz.)

The *Lycopodium-bitter* of Kamp & Bodeker reduces potassio-cupric tartrate after boiling with dilute acids, but not in its unaltered state, and should therefore perhaps be regarded as a glucoside.

*Menyanthin*, boiled with dilute sulphuric acid is resolved into sugar and an oil which smells like bitter almonds. (Ludwig, *N. Br. Arch* 108, 84.)

*Myronate of potash* is decomposed in contact with myrosyn (x, 54) and water, yielding oil of mustard, sugar, and other products. (Ludwig & Lange, *Zeitschr. Ch. Pharm.* 3, 577.) The formula  $C^{20}NH^{19}S^4O^{18}, KO$  ( $= C^8NH^5S^2 + KO, S^2O^4 + C^{12}H^{14}O^{14}$ ) given by Ludwig & Lange, is, according to Will & Körner (*Ann. Pharm.* 119, 376), more correctly  $C^{20}NH^{18}KS^4O^{20}$  and contains the elements of oil of mustard  $C^8NH^5S^2$ , glucose  $C^{12}H^{12}O^{12}$  and bisulphate of potash  $S^2KHO^8$ . Ludwig & Lange also found sulphate of potash among the products of the reaction, but no sulphite.

*Ononin* is resolved by boiling with dilute acids, into formonetin and glucose (Hlasiwetz):



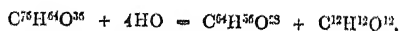
*Onospin* is resolved under similar circumstances into ononetin and sugar (Hlasiwetz):



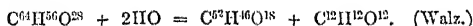
Such is the view of the reaction given by Limpricht (*Grundr. d. org. Chem.* Braunsch. 1854, 680.) For Hlasiwetz's formulæ, see *Ononin*.

The sugar formed from ononin and onospin by the action of dilute sulphuric acid, remains in solution after the second product of the decomposition has been removed by filtration, the sulphuric acid by carbonate of lead, and the excess of lead by sulphuretted hydrogen, and is obtained by evaporation as a very sweet fermentable syrup, in which granular crystals form after a few days. These crystals melt at the heat of the water-bath, to a viscid syrup, which remains soft after a day's drying and exhibits all the reactions of grape-sugar. (Hlasiwetz, *Wien. Akad. Ber.* 15, 153.) Rotatory power not examined.

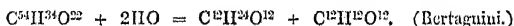
*Paristypnin* boiled with dilute sulphuric acid is resolved into paridin and sugar:



The *paridin* thus produced is resolved, by boiling with a larger quantity of dilute sulphuric acid (?), into paridol and sugar :

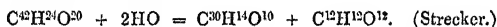


*Philyrin* is resolved by boiling with dilute hydrochloric acid into philygenin and grape-sugar; by lactic fermentation, into philygenin and the products of the decomposition of grape-sugar:

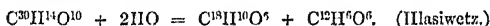


From the solution freed from philygenin and hydrochloric acid (by carbonate of lead), the sugar crystallises, after evaporation and re-solution in alcohol, in warty masses exhibiting the properties of grape-sugar. (Bertagnini, *Ann. Pharm.* 92, 110.)

*Phlorhizin* is decomposed by dilute acids, not by emulsin, yielding phloretin and sugar (Stas):



*Phloretin* boiled with alkalis is resolved into phloretic acid (xiii, 308) and phloroglucin (p. 66):

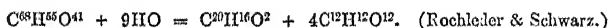


Phlorhizin-sugar is difficult to crystallise, and exhibits the properties and composition of crystallisable grape-sugar. (Stas, *Ann. Pharm.* 30, 200.) It reduces the same quantity of cupric oxide as dextro-glucose. (Rosser, *Ann. Pharm.* 74, 178.)

*Pinipicrin* splits up into icinicol and sugar when its aqueous solution is heated with acids:



*Ericolin* treated with dilute acids yields the same products in other proportions:

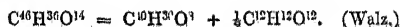


The sugar produced from pinipicrin is rendered uncrystallisable by the foreign substances contained in it; at 100° it becomes soft; at common temperature it is solid and brittle, and is easily reduced to a yellowish powder containing 2 p. c. ash, and after deduction of this, 39.06 p. c. C., 6.62 H., and 54.32 O., corresponding approximately to the formula  $\text{C}^{12}\text{H}^{12}\text{O}^{12}$ . (Kawalier, *Wien. Akad. Ber.* 11, 352.)

*Populin*, when boiled with dilute acids, splits up into benzoic acid, saliretin and glucose (Piria):



*Prophetin* is decomposed by ebullition with hydrochloric acid into propheretin and sugar:



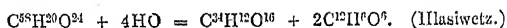
*Quercitrin* is decomposed by dilute sulphuric acid into quercetin and quercitrin-sugar (Rigaud):



Quercetin is further decomposed by boiling with potash-ley into



quercetic acid and phloroglucin (p. 65). (Illasiwetz.) The same products are obtained, but in different proportions by the decomposition of *Alpha-quercetin*:

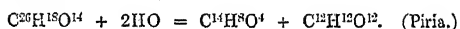


*Quercitrin-sugar* is obtained as a light-yellow syrup, which solidifies in a crystalline mass on standing for a few days over sulphuric acid, by filtering off the quercetin, separating the sulphuric acid by carbonate of baryta, evaporating on the water-bath, decolorising with animal charcoal, and again evaporating. It has a sweeter taste than dextro-glucose. Does not rotate the plane of polarisation. Dried in vacuo, it contains 34.78 p. c. C., 7.24 H., and 57.98 O., corresponding to the formula  $C^{12}H^{12}O^{12} \cdot 3HO$  (calc. : 34.65 p. c. C., 7.47 H.) When warmed with potassio-cupric tartrate, it immediately reduces the same quantity of cuprous oxide as would be reduced by dextro-glucose. (Rigaud, *Ann. Pharm.* 90, 195.)

Schunck's *Rubianic acid* splits up into alizarin and sugar when boiled with dilute sulphuric acid, or with aqueous alkalis, or by contact with water and erythrozym.  $C^{62}H^{20}O^{27} + 5HO = 2C^{14}H^{15}O^4$  (Alizarin, according to Schunck; see xiv, 137) +  $2C^{12}H^{12}O^{12}$ . — Rochleder's *Ruberythric acid*,  $C^{72}H^{40}O^{40}$  or  $C^{56}H^{31}O^{31}$ , perhaps identical with the last substance, yields the same products when heated with hydrochloric acid.  $C^{72}H^{40}O^{40} = 3C^{20}H^6O^8 + C^{12}H^{12}O^{12} + 10HO$ , or  $C^{56}H^{31}O^{31} = 2C^{20}H^6O^8 + 1\frac{1}{2}C^{12}H^{12}O^{12} + 3HO$ . (Rochleder.)

In the complicated decomposition of Schunck's *Rubian* by the same reagents and by chlorine, sugar is obtained together with various other bodies. *Rubihydran* and *Rubidehydran* behave in the same way. (Schunck.)

*Salicin* is decomposed into saligenin (xii, 233) and glucose by contact with emulsin:



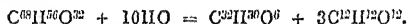
The sugar is in every respect identical with dextro-glucose. (Schmidt.) By boiling with dilute acids, saliretin is obtained in place of saligenin (xii, 232). (Piria.)

*Saponin* is decomposed into sapogenin and saponin-sugar or glucose, when boiled with dilute acids. (Overbeck; Rochleder & Schwarz, see p. 54.) See *Saponin* for the conjectural equation of decomposition.) Senegin (isomeric with saponin, according to Bolley) yields, besides sapogenin, a substance which reduces potassio-cupric tartrate. (Bolley.)

*Saponin-sugar* remains in solution after the sapogenin has been filtered off, the acid removed by carbonate or oxide of lead, and the excess of lead by hydrosulphuric acid; and, by treatment with animal charcoal and evaporation, is obtained as a tasteless, yellowish brown residue, easily soluble in water. (Rochleder & Schwarz, *Wien. Akad. Ber.* 11, 339.) — When saponin is decomposed with dilute sulphuric acid, glucose remains in solution after removal of the excess of acid, and may be obtained crystallised by evaporation. It has a sweet taste, and reduces an alkaline solution of cupric oxide in the cold. (Overbeck, *N. Br. Arch.* 77, 135.) Bolley did not succeed in determining saponin-sugar (by means of an alkaline solution of cupric oxide?). (*Ann. Pharm.* 91, 120.) Crawford obtained gum, but no sugar, from saponin, by means of dilute sulphuric acid. (*Pharm. Viertelj.* 6, 361.) — Saponin-

sugar dried at 100° contains, according to Rochleder & Schwarz, 41.99 p. c. O., 6.55 H., and 51.46 O., corresponding to the formula  $C^{12}H^{11}O^{11}$ .

*Scammony-resin* ( $C^{68}H^{51}O^{32}$ ) and *Scammonic acid* ( $C^{68}H^{56}O^{32} \cdot 3HIO$ ) split up into scammonolic acid and sugar when boiled with dilute acids (or with baryta-water):

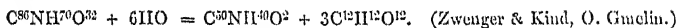


Like jalapin (p. 345), therefore, but with the difference that, instead of the product corresponding to jalappinol (which is converted by strong bases into jalappic acid), a product containing 1 at. water less is formed. (Spirgatis.—On the (highly probable) identity of scammony-resin with jalapin, see the compounds with 32 at. carbon.)

The sugar remains in solution after separation of the scammonolic and sulphuric acids, and can be obtained in sweet-tasting laminae grouped in cauliflower-like shapes, which behave like glucose with sulphate of copper and potash-ley, when heated, and when fermented. (Spirgatis, *Ann. Pharm.* 116, 305.)

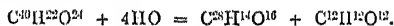
*Smilacin* is slowly decomposed when boiled with hydrochloric acid, with separation of a jelly and formation of sugar. (O. Gmelin, Delffs, Walz.)

*Solanin* splits up into solanidin and glucose, when boiled with dilute acids:

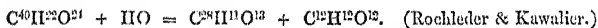


The sugar crystallises well, and possesses the reactions and compositions of dextro-glucose. (Zwenger & Kind, *Ann. Pharm.* 118, 149.) Rotatory power not determined.

*Thujin* is decomposed, by heating its alcoholic solution with dilute acids, into thujetin and sugar:

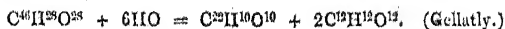


When it is heated for a shorter time, thujinenin  $C^{28}H^{12}O^{14}$  may also be formed in place of the thujetin.—Thujin, heated with baryta-water, yields thujetic acid and sugar:

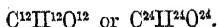


When thujin has been decomposed by acids, the sugar remains in solution after removal of the thujetin and sulphuric acid (by carbonate of baryta), and, by evaporation and drying at 100°, is obtained as a colourless mass, which is easily reduced to a white powder when cold, and contains 39.83 p. c. O., and 6.81 H., corresponding to the formula  $C^{12}H^{12}O^{12}$ ; its aqueous solution does not crystallise even after standing for several months; it reduces the same quantity of cupric oxide as dextro-glucose. The sweet sugar of the same composition, produced by the action of baryta-water, solidifies (after removal of the baryta by dilute sulphuric acid, of the excess of sulphuric acid by basic acetate of lead, and of the lead by hydrosulphuric acid) to a crystalline mass when its solution is allowed to stand a short time after evaporation on the water-bath. (Rochleder & Kawalier, *Wien. Akad. Ber.* 29, 12.)

*Xanthorhamnin* is decomposed into rhamnetin and sugar by boiling with dilute acids:



## Sorbite.



PELOUZE. *Compt. rend.* 34, 377; *N. Ann. Chim. Phys.* 35, 222; *N. J. Pharm.* 21, 321; *Ann. Pharm.* 83, 47; *J. pr. Chem.* 56, 21; *Pharm. Centr.* 1852, 257.

*Sorbite* exists in ripe mountain-ash berries, the fruit of *Sorbus Aucuparia*. (*Handbuch*, viii, *Phytochem.* 17.) Byschl (*N. Reperit.* 3, 4) did not succeed in obtaining crystals of sorbite from the juice of fresh mountain-ash berries, but found instead an amorphous, unfermentable sugar (Byschl's *amorphous sorbin*), which dissolved easily in alcohol.

*Preparation.* The expressed juice of mountain-ash berries, gathered towards the end of September, produces deposits and vegetations when left to itself for 13 or 14 months, and at last becomes clear again. The clear liquid is decanted and evaporated to a thick syrup, when it yields repeated crops of crystals, which are obtained pure by two crystallisations with help of animal charcoal.

*Properties.* Colourless, transparent, hard crystals, belonging to the rhombic or right prismatic system. *Fig.* 53 without *i* and  $\alpha$ . Rhombic prism *y*, whose edges are perpendicularly truncated by *p* and *m*; further the right terminal face *t*; between *t* and *m* the horizontal prism *u*, and between *y* and *m* a second rhombic prism *y'*. — *y*:*y* over *p* =  $142^{\circ} 53'$  (obs.); *u*:*u* over *t* =  $141^{\circ} 11'$  (obs.); *u*:*u* over *m* =  $38^{\circ} 49'$  (calc.); *y*:*y* over *m* =  $37^{\circ} 7'$  (calc.), =  $36^{\circ} 26'$  (obs.); *y*:*p* =  $161^{\circ} 26'$  (calc.); *y*:*m* =  $108^{\circ} 33'$  (calc.), =  $108^{\circ} 10'$  (obs.); *y'*:*y* =  $164^{\circ} 20'$  (obs.); *u*:*t* =  $160^{\circ} 35'$  (calc.); *u*:*m* =  $109^{\circ} 24'$  (calc.); *y*:*u* =  $96^{\circ} 4'$  (calc.), =  $96^{\circ} 32'$  (obs.) (Berthelot, *N. Ann. Chim. Phys.* 35, 222).

Grates between the teeth. As sweet as cane-sugar. Sp. gr. 1.654 at  $15^{\circ}$ . Molecular rotatory power at  $7^{\circ}$  temperature,  $[\alpha]_D = 46.9^{\circ}$ , only slightly variable with the temperature, and just as great in a freshly-prepared solution (Berthelot, *Chim. organ.* 2, 252). — Contains equal numbers of atoms of carbon, hydrogen, and oxygen: hence, no doubt, it is  $C^{12}H^{12}O^{12}$  (Pelouze).

*Decompositions.* 1. Gives off acid water when heated, and is converted after some time at  $150^{\circ}$ — $180^{\circ}$  into a dark-red mass, which consists chiefly of Pelouze's *sorbic acid*. [Not the same as Hofmann's *sorbic acid* (*Ann. Pharm.* 110, 129; *Chem. Soc. Qu. J.* 12, 43.)] On dissolving the residue, which is insoluble in water, aqueous acids, or alcohol, in aqueous ammonia or potash, a dark-brown solution is obtained, from which hydrochloric acid throws down amorphous dark-red flakes; these contain, after drying between  $120^{\circ}$  and  $150^{\circ}$ , 57.96 p. c. O., 5.51 H., and 36.53 O., corresponding, according to Pelouze, with the formula  $C^{32}H^{18}O^{15}$ . Their solution in ammonia-water gives coloured precipitates with metallic salts; with lead-salts one containing 51.35 p. c. lead-oxide, —  $C^{32}H^{18}O^{15}, 3PbO$ , according to Pelouze. — 2. Sorbite melts when quickly heated on platinum-foil, and burns away with a smell of cura-

mel.—3. Hot *nitric acid* converts it into oxalic acid (Pelouze.) Oxidising agents also produce racemic acid (x. 346) from sorbite (Des-saignes, *Bull. Soc. Chim. Paris*, 1861, 32).—4. Not altered when heated with *dilute acids*; coloured reddish-yellow by *oil of vitriol*, charred on heating. When heated for several hours with fuming *hydrochloric acid*, it is converted into humous substances in the same way as glucose (p. 315). (Berthelot, *Chim. organ.* 2, 252.)—5. Sorbite, heated to 100° with *tartaric acid*, yields a small quantity of a substance belonging to the class of saccharides (p. 316), whose lime-salt reduces potassio-cupric tartrate (Berthelot, *N. Ann. Chim. Phys.* 54, 82).—6. Becomes brown when heated with *potash-ley*, and evolves a smell of caramel. Heated with lime, hydrate of baryta, or oxide of lead, it behaves in the same way.—7. The solution of *cupric hydrate* in aqueous sorbite, and aqueous solution of sorbite mixed with *potassio-cupric tartrate*, deposit cuprous oxide when warmed or left to stand.—8. Not fermentable with *yeast* (Pelouze), not even after being heated with acids, but, when left to stand in contact with *cheese and chalk*, at 40°, it suffers a decomposition which gives rise to a large quantity of lactic acid, alcohol, and butyric acid, without previous formation of a fermentable sugar (Berthelot, *N. Ann. Chim. Phys.* 50, 350).

*Combinations.* Dissolves in about  $\frac{1}{2}$  pt. cold *water*. The saturated solution has sp. gr. 1.372 at 15°.—Forms, with *chloride of sodium*, a compound crystallising in cubes.—Aqueous sorbite dissolves *hydrate of lime* and *hydrate of baryta*. The solution of the former deposits flocks when heated, decomposition occurring at the same time.

*Sorbite with Lead-oxide.*—Aqueous sorbite dissolves oxide of lead; it does not precipitate basic acetate of lead, but on addition of ammonia throws down a white precipitate, which, while being dried, smells of caramel, and contains, on the average, 74.5 p. c. oxide of lead, 11.2 O., and 1.48 H., corresponding to the formula  $C^{12}H^{12}O_9 \cdot 4PbO$  (calculation: 74.4 p. c. lead-oxide, 12.0 O., and 1.5 H.) (Pelouze).

Aqueous sorbite dissolves *cupric hydrate*.—It is insoluble in cold, slightly soluble in boiling, *alcohol* (Pelouze).

## Inosite.



J. SCHERER. *Ann. Pharm.* 73, 322; *J. pr. Chem.* 50, 32; *Pharm. Centr.* 1850, 422; *N. J. Pharm.* 18, 71; *Lieb. Kopp. Jahresber.* 1850, 537. — *Würzb. medic. Verhandl.* 1851, 2, 212; *Ann. Pharm.* 81, 375; *J. pr. Chem.* 54, 405; *Pharm. Centr.* 1852, 192; *Lieb. Kopp. Jahresber.* 1851, 552.

VOHL. *Ann. Pharm.* 99, 125; abstr. *J. pr. Chem.* 69, 299; *N. Ann. Chim. Phys.* 48, 380. — *Ann. Pharm.* 101, 50; *J. pr. Chem.* 70, 489; *Chem. Centr.* 1857, 356; together with the first paper: *Lieb. Kopp. Jahresber.* 1856, 667. — *Ann. Pharm.* 105, 330; abstr. *J. pr. Chem.* 74, 125; *Chem. Centr.* 1858, 446; *Kopp's Jahresber.* 1858, 489.

CLOETTA. *Züricher Naturf. Verhandl.* 3, 402 and 4, 174; *Ann. Pharm.* 99, 289; *J. pr. Chem.* 66, 211 and 70, 112; abstr. *N. Ann. Chim.*

*Phys.* 46, 369; *Chem. Gaz.* 1856, 61; *Lieb. Kopp. Jahresber.* 1855, 747 and 1856, 708.

*Inosin, Phaseomannite.* Discovered by Scherer in 1850.—E. Simon, (*N. Br. Arch.* 29, 186), designates as *Phaseolin* a substance, extracted by ether from the alcoholic extract of white beans, which yields, with emulsin, a volatile oil.

*Occurrence.* In the muscle of the heart (Scherer). In the lungs, kidneys, liver, and spleen of oxen (Cloetta), also in the brain (W. Müller). In the human kidneys, and in the urine of a sufferer from Bright's disease (Cloetta). At most, to the extent of  $\frac{1}{10}$  p.c. Many other parts of the animal organism have been examined in vain for inosite. (See *Handbuch*, viii, *Zoochem.* 80, 205, 489, 512).—In green kidney-beans, the unripe fruit of *Phaseolus vulgaris* (as much as  $\frac{2}{3}$  p.c.) (Vohl).

*Preparation.* *From organs of the animal body.* 1. The muscle of the heart, or other organs containing inosite, is exhausted with water as directed (x. 250) in the case of creatine, the phosphates are precipitated from the liquid by baryta-water; the filtrate is evaporated; and the creatine allowed to crystallise out. The mother-ley is treated with dilute sulphuric acid to remove the dissolved baryta, and, after removal of the sulphate of baryta, heated as long as volatile acids escape. It is then, in order to remove the last traces of volatile acids and of lactic acid, repeatedly shaken up with ether as long as anything is taken up from it. The liquid, separated from the ether is mixed with alcohol till a turbidity begins to appear; then, after standing for some time, it is poured off from the precipitated sulphate of potash, and mixed with more alcohol, whereby crystals of inosite mixed with sulphate of potash are obtained. The crystals of the former are picked out and dissolved in a small quantity of warm water, which leaves the more difficultly soluble sulphate of potash, and are purified by recrystallisation (Scherer).—2. The fresh-chopped tissue is covered with water, and allowed to stand for 24 hours in a cool place with frequent stirring; the liquid is then separated and the residue pressed; the solution is heated with a little acetic acid to separate albumin and haematin; strained, evaporated on the water-bath to one tenth; precipitated with sugar of lead, and filtered; and the filtrate is mixed with basic acetate of lead, whereupon inosite is thrown down in combination with oxide of lead, accompanied, when these are present, by uric acid, cystin, and other substances. The precipitate, after being somewhat washed, is decomposed under water by hydrosulphuric acid, and the liquid filtered from the sulphide of lead; it then sometimes deposits crystals of uric acid, and when evaporated to a small bulk on the water-bath, and mixed with alcohol till a turbidity is produced, it yields crystals of inosite (Cloetta). Sugar of lead may also be added at once to the water used for making the extract (W. Müller).—3. The liquid from which the inosite is to be separated is concentrated by evaporation, and mixed, boiling, with three or four measures of alcohol; if a large precipitate, which sticks to the bottom, is thus produced, the liquid is poured off hot, but if only a slight, not sticky, precipitate is produced, the hot solution is filtered through a previously heated funnel, and left to stand for 24 hours, when crystals of inosite are deposited, and are

washed with a small quantity of cold alcohol. If the precipitate caused by hot alcohol is dissolved in a small quantity of boiling water, and treated like the first solution, a further quantity of inosite is obtained. — In case no inosite separates from the cooled solution, the crystallisation may be facilitated by adding ether till a turbidity remains after shaking (Cooper Lane, *Ann. Pharm.* 117, 118).

*From French beans.* — The fruit cut up in the bean-mill is hung in a pressing bag for half an hour in boiling water, or in steam, whereby it is rendered fit for pressing; the expressed liquid is then evaporated to a syrup on a water-bath, and alcohol is added till a permanent turbidity is produced. The crystals which form are purified by repeated crystallisation from water with help of animal charcoal (Vohl). Vohl formerly destroyed the sugar of the beans by fermentation at the beginning.

*Properties.* Anhydrous inosite is obtained by drying crystallised inosite at 100° or in vacuo, as a white effloresced mass, which melts only at a temperature exceeding 210°,—then yielding a colourless liquid, which solidifies in the crystalline state when quickly cooled, and to an amorphous mass when cooled slowly,—but does not lose weight or undergo further alteration (Scherer). White, opaque crystals of anhydrous inosite separate when the aqueous solution is cooled below 0°. (Vohl.) Tastes purely sweet. Has no rotatory power. (Vohl.)

	at 100°, or in vacuo.			Scherer.			Vohl.			Cloetta.		
12 C .....	72	...	40.00	...	40.12	.....	40.03	...	40.00	...	40.00	...
12 H .....	12	...	6.67	...	6.69	.....	6.68	...	6.71	...	6.71	...
12 O .....	96	...	53.33	...	53.19	.....	53.29	...	53.29	...	53.29	...
$C_6H_{12}O_{12}$ .....	180	...	100.00	...	100.00	.....	100.00	...	100.00	...	100.00	...

Vohl examined inosite from beans.

*Decompositions.* 1. After dehydrated inosite has been melted above 210°, it swells up when more strongly heated, and evolves gas which burns with a pale blue flame; it is afterwards charred, and then burns with a brightly luminous flame, leaving an easily combustible cinder. (Scherer.) When quickly heated, it gives off vapours which excite tears and produces a smell of burnt sugar. (Vohl.)—2. Aqueous inosite is not affected by ozone. (Görup-Besanez, *Ann. Pharm.* 110, 103.)—3. The solution of inosite in dilute nitric acid does not give off nitrous acid till moderately concentrated, and, after evaporation to dryness, contains oxalic acid. The aqueous solution of the residue, freed from oxalic acid by carbonate of lime, deposits, on standing, magnificent purple-red flocks, soluble in dilute acids and precipitable without alteration by ammonia. (Vohl.) When aqueous inosite is evaporated nearly to dryness with nitric acid, the residue, moistened with ammonia and a small quantity of solution of chloride of calcium, and again evaporated, leaves a rose-coloured residue. (Scherer, Vohl.) Inosite dissolves without evolution of gas in cold or boiling nitric acid of sp. gr. 1.52, forming a solution whence oil of vitriol precipitates nitro-inosite. (Vohl.)—4. Dissolves without coloration in cold oil of vitriol, or in oil of vitriol heated to 100°, and is not blackened till more strongly heated, and then evolves sulphurous acid. (Vohl.) Inosite is not altered by boiling with dilute acids. (Scherer, Vohl.)—5. May be boiled with concentrated potash-ley, or with baryta-water, without alteration or coloration. (Scherer, Vohl.)—6. The aqueous solution mixed with cupric

*sulphate* yields, on addition of potash-ley, a bluish green precipitate which quickly disappears on addition of excess of potash. No cuprous oxide separates from the solution on boiling, but a light blue precipitate falls when the liquid is left to stand for several days. (Scherer.) Aqueous inosite yields, when heated with *potassio-cupric tartrate*, a green solution, whence a bulky green precipitate separates, the supernatant liquid again becoming blue. After removing the precipitate, the filtrate shows the same change of colour when heated. (Cloetta.) The change of colour, which occurs on heating the deep azure-blue mixture of inosite and potassio-cupric tartrate, is not remarkable, and is due, as well as the production of the precipitate, to the presence of traces of foreign substances. (Vohl.)—7. Inosite is not capable of undergoing vinous fermentation. (Scherer.) In contact with *cheese, flesh*, or decaying *membrane*, and chalk, it undergoes lactic fermentation, carbonic, lactic, and butyric acids being formed. (Scherer, Vohl.)

*Combinations.* — With Water. — *Hydrated Inosite*,  $C^{12}H^{12}O^{12}, 4H_2O$ . Obtained from concentrated solutions, in tabular crystals resembling gypsum, an inch long and several lines broad. (Vohl.) Oblique prismatic crystals, for the most part in cauliflower-like groups. (Scherer.) Prisms belonging to the right prismatic system, with angles of  $138^{\circ} 52'$  and  $41^{\circ} 8'$ . (Cloetta.) Sp. gr. 1.1154 at  $5^{\circ}$ . (Vohl.) The crystals become white and opaque in dry air, in vacuo over sulphuric acid, or at  $100^{\circ}$ , and lose 16.6 p. c. water of crystallisation (4 at. = 16.66 p. c.), being converted into anhydrous inosite. (Scherer, Vohl, Cloetta.)

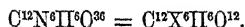
Hydrated inosite dissolves in 6 pts. water at  $19^{\circ}$  (Vohl), in  $6\frac{1}{2}$  pts. at  $24^{\circ}$  (Cloetta). The concentrated solution, of sp. gr. 1.0548 at  $19^{\circ}$ , is not syrupy, and not subject to spontaneous decomposition. (Vohl.)

Aqueous inosite dissolves *chloride of sodium* and *chloride of potassium*, which crystallises out alone on evaporation. (Vohl.)

Solution of inosite does not precipitate solution of *sugar of lead*. *Basic acetate of lead* throws down from aqueous inosite a transparent jelly, which after a few moments becomes pasty and white, and dries up, after being washed with water and alcohol, to a yellow pulverisable mass, which at  $100^{\circ}$ , contains 76.5 p. c. oxide of lead, corresponding to the formula  $C^{12}H^{12}O^{12}, 5PbO$  (calculation: 75.6 p. c. lead oxide). (Cloetta.) The formula  $C^{12}H^{11}PbO^{12}, 4PbO$ , which contains 1 at. water less, agrees better. [Kr.] Vohl got no lead-salt of constant composition.

Slightly soluble in cold aqueous *alcohol*, more soluble at the boiling heat; insoluble in absolute alcohol. Does not dissolve in *ether*.

### Nitro-inosite.



VOHL. *loc. cit.*

#### *Inosine hexanitrique.*

Dehydrated inosite is dissolved in nitric acid of sp. gr. 1.52 and the solution is precipitated with oil of vitriol. The product, which, according to the temperature retained by the mixture, separates either as powder or as oil-drops which solidify to crystalline masses, is well washed with water and recrystallised from boiling alcohol.

Rhombohedral, often some lines in length. Melts to an oil when heated, and solidifies to an amorphous mass which becomes crystalline after a few days. Permanent in dry or moist air.

					Vohl.
12 C .....	72	...	16.00	.....	16.08
6 N .....	84	...	18.67	.....	18.58
6 H .....	6	...	1.33	.....	1.41
36 O .....	288	...	64.00	.....	63.93
<hr/>					
C <sup>12</sup> X <sup>6</sup> 11 <sup>6</sup> O <sup>18</sup> .....	450	...	100.00	.....	100.00

Deflagrates without residue when quickly heated, and detonates under the hammer.—Decomposed when warmed with concentrated acids—Dissolves with dark brown colour and evolution of ammonia in cold or warm *potash-ley*. The alkaline solution precipitates cuprous oxide from *potassio-cupric tartrate*, and a mirror of metallic silver from *ammonio-nitrate of silver*.—Nitro-inosite treated with nitric acid, ammonia and chloride of calcium shows the coloration of inosite (p. 353).

Insoluble in *water*; dissolves easily in *alcohol*.

### Scyllite.

STÄDELER & FRERICHS. *J. pr. Chem.* 73, 48; *Chem. Centr.* 1858, 372; *Chem. Gaz.* 1858, 281; *Kopp's Jahresber.* 1858, 550.

*Occurrence.* Most abundantly in the kidneys of the ray and shark, also in the liver and spleen of the former and in the liver and gills of the latter. In the kidneys of the prickly dog-fish.

*Preparation.* The organs of the above-mentioned fishes, triturated with coarsely-powdered glass, are stirred up with 1½ to 2 measures of alcohol, and pressed, the residue is treated again with a small quantity of alcohol, and the extracts are filtered and evaporated. The residue is dissolved in water; the fat and undissolved gelatinous matter are filtered off; and the filtrate is evaporated to a syrup, covered with hot absolute alcohol, and left to stand for 24 hours, whereby urea, sometimes also leucine, tyrosine, and other bodies pass into solution, while a brown mass separates out. This is dissolved in water and left to evaporate spontaneously until crystals have separated, which are then removed from the mother-ley and freed from the chloride of sodium, which has also crystallised out, by mechanical selection. The crystals, which are either taurine or scyllite, or a mixture of both, are treated with basic acetate of lead in moderately concentrated solution, and so yield the insoluble lead-compound of scyllite, which is decomposed under water by hydrosulphuric acid. The scyllite is obtained crystallised by evaporating the solution filtered from the sulphide of lead, or by slowly adding alcohol to it.

*Properties.* Isolated, well-developed prisms or tables, possessing a strong vitreous lustre, belonging to the oblique prismatic system, the base abutting on the acute edge; when rapidly formed, they resemble inosite. Taste, slightly sweet. Permanent in the air. Neutral.



*Decompositions.* Melts with difficulty when heated in a glass tube, swells up when charred, and evolves acid vapours and a smell of caramel. — Burns with flame upon platinum foil, leaving an easily combustible charcoal.—Not altered by oil of vitriol, either cold or slightly warm; decomposed when heated, with evolution of sulphurous acid, the solution acquiring a yellow, and at last a red-brown colour.—Does not colour boiling soda-ley, or reduce alkaline cupric solutions.—With nitric acid, ammoniac and chloride of calcium, it does not behave in the same way as inosite (p. 353).

Less soluble in water than inosite. Insoluble in cold nitric acid of sp. gr. 1.3; dissolves slowly in the same acid when boiling, and is precipitated without alteration by alcohol.—Sugar of lead does not precipitate its aqueous solution; basic acetate of lead throws down a pasty precipitate. Insoluble in alcohol, and precipitable thereby from its aqueous solution.

*Saccharoïdal Substances  $C^{12}H^{14}O^{12}$ .*

**Mannite.**



- PROUST. *N. Gehl.* 2, 83; *Ann. Chim.* 57, 143.  
 BUCHHOLZ. *Taschenbuch*, 1809, 150.  
 A. VOGEL. *Schw.* 37, 365.  
 BRENDENCKE. *N. Br. Arch.* 16, 49.  
 FAVRE. *N. Ann. Chim. Phys.* 11, 71; *J. pr. Chem.* 32, 362.  
 KNOP & SCHNEIDERMAN. *Ann. Pharm.* 49, 243. — *Ann. Pharm.* 51, 132; *J. pr. Chem.* 32, 411.  
 LEUCHTWEISS. *Ann. Pharm.* 53, 128.  
 STRECKER. *Ann. Pharm.* 73, 68.—92, 80.  
 A. KNOP. *Pharm. Centr.* 1849, 801.—1850, 49; *Ann. Pharm.* 74, 347; *J. pr. Chem.* 48, 362.  
 BEITHÉLOT. Combinations with acids: *Compt. rend.* 42, 1111; *J. pr. Chem.* 69, 450; *Chem. Centr.* 1856, 625; in detail: *N. Ann. Chim. Phys.* 47, 297; abstr. *Lieb. Kopp. Jahresber.* 1856, 652.—Fermentation: *Compt. rend.* 43, 238; *N. J. Pharm.* 30, 269; *J. pr. Chem.* 69, 454; *Chem. Centr.* 1856, 749; in detail: *N. Ann. Chim. Phys.* 50, 322; abstr. *Lieb. Kopp. Jahresber.* 1856, 664; and *Kopp's Jahresber.* 1857, 509.—Occurrence: *N. Ann. Chim. Phys.* 46, 83.—Solubility of Lime in Mannite, *N. Ann. Chim. Phys.* 46, 173 — *Chimie organique*, Paris, 1860, vol. 2.  
 UBALDINI. *Compt. rend.* 45, 1016; *N. J. Pharm.* 37, 56; *J. pr. Chem.* 74, 221; *Chem. Centr.* 1858, 175; in detail: *N. Ann. Chim. Phys.* 57, 213; *Cimento*, 7, 113.  
 DE LUCA. *Compt. rend.* 47, 295; *N. J. Pharm.* 34, 353; *J. pr. Chem.* 77, 457.  
 GORUP-BESANEZ. *Ann. Pharm.* 118, 257.  
 ERLLENMEYER & WANKLYN. *Zeitschr. Ch. Pharm.* 4, 606; *Proc. Roy. Soc.* 11, 447.  
 LINNEMANN. *Ann. Pharm.* 123, 136.

*Manna-sugar, Mannazucker.*—Discovered in 1806 by Proust.—A con-

stituent of the manna which exudes from *Fraxinus rotundifolia*, *F. Ornus* and *F. excelsior*; according to Leuchtweiss (*Ann. Pharm.* 53, 127), it forms 42.6 p. c. of *Manna canellata*, 37.6 p. c. of *M. canellata in fragmentis*, 32 p. c. of *M. calabrana*.—It is found in the manna from the Cape Verd Islands (Berthelot); in the manna of the spindle-tree, produced by the punctures of *Aphis Evonymi* (Lassaigne, *J. Pharm.* 4, 526); in the honey-dew of the lime-tree (Langlois, *J. pr. Chem.* 29, 444; Reinsch, *Jahrb. pr. Pharm.* 14, 153); in *Lactucarium* (Ludwig, *N. Br. Arch.* 50, 1; Aubergier).—It remains doubtful whether mannite is contained in: the manna of *Pinus picea*, which, according to Bärwinkel (*Berl. Jahrb.* 26, 1, 191) behaves like ash-tree manna; in the honey-dew which, according to Wahlenberg, exudes from the leaves of *Hedysarum Alhagi*, of various oriental oaks, *Ficus bengalensis*, *Plumix daetylifera*, *Acer plantanoides*; in the manna which exudes from the young twigs of *Quercus bengalensis*, from the trunk and boughs of *Ceratonia Siliqua*, and from *Heracleum sibiricum* and various species of *Carex* when dried.—For the composition of the manna of Sinai and that of Kurdistan, see page 241.

The following plants and parts of plants contain mannite ready formed: the roots of *Aconitum Napellus* (T. & H. Smith, *Pharm. J. Trans.* 10, 124; *Lieb. Kopp. Jahresber.* 1850, 535), of celery, from *Apium graveolens* (Hübner, *N. Tr.* 4, 1, 308; Payen, *Ann. Chim. Phys.* 55, 219); of *Meum athamanticum* (Reinsch, *Jahrb. pr. Pharm.* 14, 389); of *Oenanthe crocata* (*Handbuch*, viii. *Phytochem.* 46); of *Polypodium vulgare* (Desfosses, *ibid.* 92); of *Scorzonera hispanica* (Witting, *N. Br. Arch.* 105, 286); the root-bark of *Tunica Granatum* [constituting Latour's *Granatin*. (*J. Pharm.* 17, 513 and 601)]. (Mitouard, Boutron-Charlard & Guillemette, *J. Pharm.* 21, 169; *Ann. Pharm.* 14, 221); the roots of *Triticum repens*. (Völcker.) The mannite existing in the extract of the last-named root was distinguished by Pfaff (*Mat. med.* 6, 110) as *grass-root sugar* (*Graswurzelzucker*); it is perhaps not always present, wherefore Stenhouse (*Ann. Pharm.* 51, 354) did not find any; sometimes however it exists in considerable quantities. (Völcker, *Ann. Pharm.* 59, 380.)—The bark of *Canella alba* (*Handbuch*, viii. *Phytochem.* 27) contains about 8 p. c. of mannite (W. Mayer & Reiche, *Ann. Pharm.* 47, 234), not, as supposed by Petros & Robinet (*J. Pharm.* 8, 198), a peculiar kind of sugar; that of *Fraxinus excelsior* contains mannite [Keller's *Fraxinin* (*Repert.* 44, 438)]. (Rochleder & Schwarz, *Ann. Pharm.* 87, 198; Stenhouse, *Ann. Pharm.* 91, 255.)—The leaves (Roussin, *J. Chim. méd.* 27, 754) and young twigs of *Syringa vulgaris* contain mannite [which, mixed with *Lilacin*, constitutes Bernays' *Syringin* (*Repert.* 24, 348)], (Ludwig, *N. Br. Arch.* 91, 289); also the leaves of *Ligustrum vulgare* (Polex; Kromayer, *N. Br. Arch.* 101, 281), celery-leaves (Vogel), the foliage of *Cocos nucifera* (Bizio, *J. Pharm.* 19, 455); the fruit of *Laurus Persea* (Avequin, *Ann. Pharm.* 32, 313; Melsens, *Ann. Chim. Phys.* 72, 109), of *Cactus opuntia* (De Luca, *Cimento*, 3, 407).—Coffee-beans contain mannite, according to Döbereiner (*N. Br. Arch.* 43, 27). Ergot of one year contained mannite, that of another year mycose (p. 301). (Mitscherlich.)—Many fungi contain mannite (see p. 301; also *Handbuch*, viii. *Phytochem.* 97).—On *algæ* (*Handbuch*, viii. *Phytochem.* 93) there is often found an efflorescence of mannite (Vauquelin, Gaultier de Claubry), which, according to Stenhouse (*Ann. Pharm.* 51, 349) may also be obtained from the dry *algæ*; according to Phipson (*Compt. rend.* 43, 1056; *Chem. Centr.* 1857, 77), mannite does not exist in fresh *algæ*, but is formed, according to him and to Soubeiran (*N. J. Pharm.* 31, 219), from vegetable mucilage by fermentation.

Gmelin is also inclined to regard as mannite, Hünefeld's *Primulin* (*J. pr. Chem.* 7, 58; *N. Br. Arch.* 8, 249) obtained from the roots of *Primula veris*.

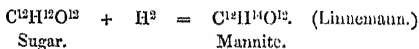
**Formation.** Under the influence of the peculiar ferment which excites mucous fermentation, cane-sugar (and therefore no doubt also dextro- and lævo-glucose) splits up into mannite, carbonic acid, and gun. (Pasteur, *Bull. Soc. Chim. Paris*, 1861, 30; see p. 280).

Mannite can be obtained after fermentation from vegetable juices which previously did not contain any. (Fourcroy & Vauquelin; Pelouze, *Ann. Chim. Phys.* 47, 411.) No mannite is formed when the sugar of carrot-juice ferments by itself, but when the pectin-substances are left in it, the juice gets thick, like white of egg, and produces mannite. (Vauquelin.) The presence of mannite after fermentation has been observed in the juice of onions (Fourcroy & Vauquelin, *Ann. Chim.* 65, 166; *N. Gehl.* 5, 357); in mangold-wurzel juice (Braconnot, *Ann. Chim.* 85, 95; Jules Gay-Lussac & Pelouze, see xi, 478); in extract of jalap-root (Herberger, *Jahrb. pr. Pharm.* 4, 8); in the juice of the tubers of *Helianthus tuberosus* (Braconnot); of *Cyclamen europæum* (De Luca, *Compt. rend.* 47, 296); in the aqueous extract of the roots of *Taraxacum officinale* (Frickhinger, *Repert.* 73, 55; T. & H. Smith, *J. Chim. méd.* 26, 135); further, in lactic fermentation (Boutron & Fremy, see xi, 473; Bensch, *Ann. Pharm.* 61, 174); in the preparation of lactic acid by Bensch's process (xi, 475), if the fermentation has gone on between  $0^{\circ}$  and  $20^{\circ}$  (Strecker, *Ann. Pharm.* 92, 80); in the fermentation of honey (Guibourt, *Ann. Chim. Phys.* 16, 371).

Mannite exists in cider after the vinous fermentation has had its regular course; it is perhaps present, ready-formed, in the apples. (Berthelot.)

The sugar which results from the decomposition of kinovin by alcoholic hydrochloric acid is identical with, or allied to, mannitan. (Hlasiwetz.—See page 345.)—According to Fremy (*J. pr. Chem.* 8, 197), mannite is produced by boiling starch with acids, and may be extracted by alcohol from the dextro-glucose.

From inverse-sugar, by the action of sodium-amalgam on its neutral aqueous solution:



**Preparation. From Manna.** 1. Manna is dissolved in 3 pts. water, the solution precipitated with basic acetate of lead; the lead removed from the filtrate by hydrosulphuric acid; the solution evaporated to a syrup after separation of the sulphide of lead, and the syrup poured into hot alcohol: mannite then crystallises out on cooling. (Bonsall, *N. Br. Arch.* 84, 70.)—2. Fermenting yeast is added to the aqueous solution of manna, in order to destroy the sugar contained in it; and the liquid is decolorised with animal charcoal when the fermentation is complete, and then evaporated to the crystallising point, the crystals being purified by recrystallisation from boiling alcohol of 82 p. c. (Leuchtweiss.)—3. Manna is dissolved in half its weight of rain-water; the solution is clarified with white of egg, and strained boiling hot through a woollen bag; the crystalline mass obtained on cooling is stirred up to a pulp, drained and pressed; and the liquid that runs away is concentrated and treated in the same way. The cake of

mannite so obtained is purified by being stirred up with water to a thick pulp, the liquid is allowed to drain away, and what is left is pressed out; the remaining mannite is dissolved in 6 or 7 pts. of hot water, and the solution treated with animal charcoal, filtered hot, evaporated, and left to crystallise (Ruspini, *Ann. Pharm.* 65, 203; *Lieb. Kopp. Jahresber.* 1847 and 1848, 793).—4. Manna is boiled with aqueous alcohol, the solution is filtered hot, and the crystals which separate are purified by crystallisation from water or alcohol (Proust.) The manna contained in fermented liquids is obtained by exhausting the extract with alcohol, after previously removing, when necessary, the substances precipitable by basic acetate of lead.

*Properties.* Long prisms or needles, more rarely short prisms belonging to the rhombic or right prismatic system, sometimes grouped together in bunches, united into sheaves, or arranged in stars. Commonly a rhombic prism  $y$  (*Fig.* 53), whose acute lateral edges are truncated perpendicularly by  $m$ , the summits being bevelled by  $u$ ; or a rhombic prism  $y$ , whose acute edges are perpendicularly truncated by  $m$ , and obtuse edges by  $p$ ; between  $y$  and  $m$  a second prism  $y'$ , and besides the bevelling face  $u$ , a second horizontal prism  $u'$  between  $u$  and  $m$ .  $u' : u'$  (above) =  $125^\circ 3'$  (observed);  $u' : u'$  (over  $m$ ) =  $54^\circ 57'$  (calculated);  $m : u' = 117^\circ 28'5$  (calc.), =  $117^\circ 26'5$  (obs.);  $y : y$  (over  $m$ ) =  $50^\circ 31'$  (obs.);  $y : y$  (over  $p$ ) =  $129^\circ 29'$  (calc.);  $m : y = 115^\circ 15'5$  (calc.), =  $115^\circ 18'$  (obs.);  $q : y = 154^\circ 44'5$  (calc.);  $m : u = 104^\circ 36'$  (calc.);  $u : u$  (above) =  $150^\circ 48'$  (obs.);  $u : u' = 167^\circ 8'5$  (obs.);  $p : y = 136^\circ 40'5$  (obs.);  $m : y' = 133^\circ 19'5$  (obs.);  $y : y' = 86^\circ 39'$  (obs.).—Different vertical prisms occur in other crystals, whereon Schabus observed the following angles:— $m : y'' = 103^\circ 10'$ ;  $p : y''' = 139^\circ 45'$ ;  $m : y'' = 163^\circ 4'$ ;  $p : y'' = 173^\circ 20'$ . The surface of the acicular crystals smooth and even; the vertical faces of the prismatic crystals, with the exception of  $y$ ,  $m$ , and  $p$ , vertically striated. Cleavage very perfect parallel to  $m$ , less perfect parallel to  $p$ , perpendicular to these directions very slight. Fracture conchoidal. Lustre vitreous on  $u$  and  $u'$ , pearly on  $m$ ; the vertical prisms have a pearly vitreous lustre. Transparent, semi-transparent, colourless to white. Streak white. Hardness = 2.5. (Schabus, *Krystallgest.* Wien, 1855, 87.)

Melts at  $166^\circ$  (Favre),  $164^\circ$  to  $165^\circ$  (De Luca),  $165^\circ$  (Berthelot), between  $165^\circ$  and  $166^\circ$  (Linnemann), and solidifies (at  $162^\circ$ : Favre) when cooled below  $140^\circ$ , to a crystalline mass. Volatilises slowly when kept melted, and sublimes without alteration; enters into ebullition at about  $200^\circ$ , part subliming or distilling over with the water, and part being converted into mannitan, most of it, however, remaining unchanged. Small quantities can be volatilised almost completely on platinum foil. Does not diminish in weight when heated for a long time to  $120^\circ$ . (Berthelot.) Tastes slightly and agreeably sweet. Acts as a purgative. (Vogel.) Becomes luminous by friction. (Bonastre, *J. Pharm.* 19, 632.) Neutral.—Has no rotatory power. (Biot, *Compt. rend.* 10, 49; Ventzke.)

			Prout.	Liebig.	Kircher.	Knop & Linne- Schnedermann.	mann.
12 C	72	39.56	38.70	39.42	39.37	39.67	39.52
14 H	14	7.69	8.81	7.71	7.90	7.69	7.87
12 O	96	52.75	54.49	52.87	52.73	52.64	52.61
$C^{12}H^{14}O^{12}$	182	100.00	100.00	100.00	100.00	100.00	100.00

Saussure, Oppermann (*Pogg.* 23, 443), and many others, have also analysed mannite. Liebig (*Ann. Pharm.* 9, 23) calculated the true formula from Oppermann's analyses, and it was definitely established by Strecker's analyses of nitro-mannite. Earlier formulæ:  $C^{15}H^{16}O^{15}$  (Proust),  $C^7H^9O^8$  (Saussure),  $C^8H^{10}O^8$  (Knop & Schneidermann). Instead of the above formula, some chemists adopt half its value  $C^6H^7O^6$ .

*Decompositions.* 1. See above. When heated, mannite does not swell up below  $250^\circ$ ; it afterwards decomposes, and burns away in contact with the air with flame and a smell of caramel, and leaves a delicate, soft, and lustreless charcoal. — On dry distillation, it evolves a smell of acrolein. (Redtenbacher, *Ann. Pharm.* 47, 148.) — 2. Manna, which, when fresh and pure is unfermentable, becomes when kept, translucent, sticky, and deliquescent in the air, and is then fermentable. (Lhermite, *Compt. rend.* 34, 114.) Berthelot (*N. Ann. Chim. Phys.* 50, 333) also found in manna 10 to 15 p. c. sugar, which did not increase in quantity by keeping in a moist, dark place.

3. A mixture of mannite and platinum-sponge, in contact with air between  $30^\circ$  and  $40^\circ$ , soon acquires an acid reaction, evolves carbonic and formic acids, and contains mannitic acid, mannitose (p. 339), and a product allied to mannitan. (Gorup-Besanez.) At higher temperatures coloured decomposition-products of mannitic acid, and perhaps also saccharic acid, are produced; if the mixture gets dry, it may become red-hot. When a concentrated aqueous solution of mannite is dropped on platinum-sponge, heat is evolved, and white clouds formed, while an odour of caramel becomes perceptible and volatile acids are produced. (Gorup-Besanez.) The products first formed are completely decomposed into carbonic acid and water by the further action of oxygen. (Döbereiner, *J. pr. Chem.* 28, 498; 29, 452. — See also Backhaus, *N. R. rept.* 9, 283.)

4. Nitric acid converts mannite into saccharic and oxalic acids, without producing mucic acid (Scheele, Fourcroy & Vanquelin, Buchholz). Mannite dissolves in nitric acid without coloration or evolution of gas; and when the solution is warmed until reddish-yellow vapours are given off, a tumultuous evolution of gas sets in, even after removal of the fire, and continues for about half-an-hour; after it has ceased, the liquid contains neither mannite nor saccharic acid, but an acid which forms, with bases, salts similar to, or identical with, those of mannitic acid. A fermentable sugar, probably mannitose (p. 339), is formed at the same time (Gorup-Besanez). When mannite is heated with nitric acid, according to Liebig's method (See Milk-sugar, p. 220), racemic acid is formed, but in smaller quantity than when dulcite is similarly treated, and is not accompanied by a trace of tartaric or antitartaric acid (x. 365), but by a very small quantity of an acid agreeing in its properties with mucic acid (Carlet, *Compt. rend.* 53, 343. — See also Dulcite.) Proust and Thénard (*N. Gehl.* 2, 217) believed they had obtained mucic acid from mannite, the latter to the extent of about 50 p. c. According to Backhaus (*N. Rept.* 9, 289), who could not obtain any tartaric acid from 1 pound of mannite, the mucic acid proceeds from the gum of the manna, which, when the mannite is incompletely purified, adheres obstinately to it.

5. Mannite distilled with peroxide of manganese and dilute sulphuric acid, evolves carbonic acid, while acrolein and formic acid pass over in the distillate (Backhaus, *N. Rept.* 9, 289). — 6. Mannite takes fire when triturated with 6 pts. peroxide of lead (Böttger). Heated with per-

oxide of lead and water, it yields formic acid, gum, and an acetyl-like substance (Döbereiner, *J. pr. Chem.* 28, 498); only a little carbonic acid is evolved, but on addition of sulphuric acid, formic acid distils over (Leuchtweiss). When mannite is mixed with *bichromate of potash* and *sulphuric acid*, carbonic acid and aqueous formic acid are given off (Leuchtweiss).

7. Distilled with excess of concentrated *hydriodic acid* (b. p. 125°), in a stream of carbonic acid, it yields iodide of hexyl.

$C^{12}H^{14}O^{12} + 11HI = C^{12}H^{13}I + 12HO + I^{10}$  (96 grm. mannite gave 83 grm. iodide of hexyl.) (Erlenmeyer & Wanklyn).

8. On heating a mixture of equal atoms of mannite and *biniodide of phosphorus* to a little above the melting point of the latter, great heat is disengaged, so that, even with small quantities, incandescence may take place, and vapours of iodine and of hydriodic acid are evolved, while an aqueous and oily distillate passes over, and charcoal remains. If broken glass is added to the mixture in order to moderate the action, and it is heated by small quantities at a time until the reaction commences, the product being then covered with water and distilled, there passes over with the aqueous vapour a heavy oil, coloured by free iodine, and possessing a burning, sweet taste and aromatic smell. After removal of the free iodine and water, this oil begins to boil at a comparatively low temperature: the boiling point, however, soon rises, and the oil passes over in part at 170°, iodine being liberated, and contains, on an average, 3.474 p. c. C., 6.14 H., and 59.12 I., corresponding nearly to a mixture of iodides  $C^{12}H^{13}I$ . [Iodide of hexyl,  $C^{12}H^{13}I$  (see decomposition 7) contains 33.96 C., 6.13 H. and 59.91 I. (W.)] Heated to 100° with oxide of silver, it is converted, in a few hours, into a non-iodised oil of variable boiling-point (the part which distils between 75° and 130°, contains 62.8 p. c. C., 10.7 H., and 26.5 O.; that which distils between 150° and 200°, contains 74.66 p. c. C., 13.14 H., and 12.20 O.—), which yields, with oil of vitriol, a conjugated acid, and acid products by oxidation (Buttlerow, *Chem. Centr.* 1857, 393). Hence Buttlerow thinks it probable that compounds of the formulæ  $C^{12}H^{13}I$  and  $C^{12}H^{14}I^2$  are mixed with the iodised oil, and regards the oil freed from iodine as a mixture of ethers containing oxygen in place of the iodine. More recently he detected iodide of methylene,  $C^2H^2I^2$ , among the constituents of the iodised oil, inasmuch as dioxymethylene,  $C^4H^4O^4$  (which is produced by the action of iodide of methylene on oxalate of silver) occurs among the products of the action of oxalate of silver upon it (Buttlerow, *Ann. Pharm.* 111, 247). — 9. On heating mannite with *bromine* and water in a sealed tube, hydrobromic acid is produced, causing the liquid to become dark-brown soon after the disappearance of the bromine, and humous substances to be formed (Barth & Illasiwetz, *Ann. Pharm.* 122, 111).

10. Mannite, heated for several hours to 150° with syrupy aqueous *phosphoric acid*, yields a small quantity of manni-phosphoric acid, the lime-salt of which may be obtained as a jelly by dissolving the product in water, neutralising with chalk, and precipitating the filtrate with alcohol (Berthelot). — 11. By dissolving mannite in oil of vitriol, manni-bisulphuric acid and manni-tersulphuric acid are produced. (See below.) The solution does not blacken even when heated to 100°.—

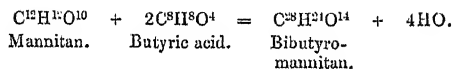
12. Mannite dissolves, without evolution of gas, in fuming *nitric acid*; oil of vitriol throws down from the solution nitromannite (Domonte & Ménard, Strecker).—13. Mannite scarcely absorbs *hydrochloric acid* gas even at  $100^{\circ}$ , but when long heated to  $100^{\circ}$  with fuming aqueous hydrochloric acid, in a sealed tube, it yields chlorhydro-mannitan, and, by several days' boiling, mannitan (Berthelot).—14. Moist *arsenic acid* colours mannite brick-red in a few days (Elsner, *Schw.* 50, 348).

Mannite combines with mono-, bi-, and ter-basic acids, with elimination of water, forming the *mannitanides*, a class of compounds corresponding to the mono-saccharides (p. 316), in which the properties of the acid and of mannite are concealed, but which are capable of undergoing decomposition by taking up again part of the eliminated water, so as to yield the original acid and mannitan (Berthelot).

The mannitanides are obtained from the acids and mannite, sometimes by merely bringing them together at common temperatures or at  $100^{\circ}$ , but more commonly by heating them for a long time to  $200^{\circ}$  or  $250^{\circ}$ ; never more than part of the acid and of the mannite enters into combination, the greater portion of both remaining uncombined.—The mannitanides resemble the natural fats, and are decomposable by water at  $240^{\circ}$ , or by alkalis at  $100^{\circ}$ , for the most part, however, only with difficulty and by long-continued action. In all such cases it is mannitan that separates out, except that, by further fixation of water, a portion of it is converted into mannite. In this respect, and so far as regards the quantity of water separated in the formation of the mannitanides, it is mannitan (and not mannite) that is an analogue of alcohol (Berthelot).

A. Mannite and *monobasic acids* furnish three distinct classes of compounds.

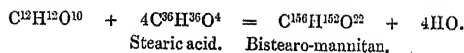
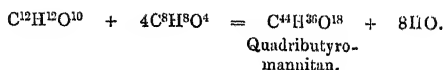
a. Formed by the combination of 1 at. mannitan with 2 at. acid and elimination of 4 at. water.



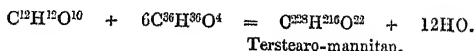
Berthelot also reckons chlorhydro-mannitan as belonging to this class:



b. From 1 at. mannitan and 4 at. acid, with elimination of 4 or 8 at. water:



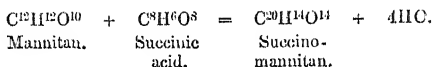
c. From 1 at. mannitan and 6 at. acid, with elimination of 6 at. water.



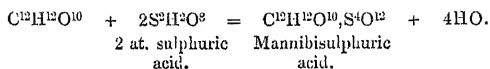
B. The compounds produced by heating mannite with *bibasic acids* are formed, according to Berthelot,—

a. From 1 at. mannitan and 1 at. acid, with elimination of 4 at. water.

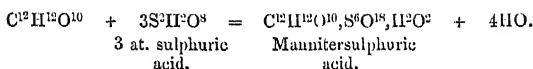
Berthelot classes here kinovin (p. 345), from whose formula he deducts 2 at. water given off between 160° and 180°. Van Bemmelen's succino-mannitan belongs to this class:



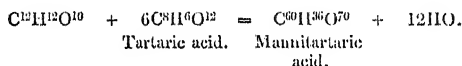
b. From 1 at. mannitan and 2 at. acid, with elimination of 4 at. water:



c. From 1 at. mannitan and 3 at. acid, with elimination of 4 at. water:

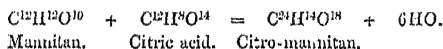


d. From 1 at. mannitan and 6 at. acid, with elimination of 12 at. water:

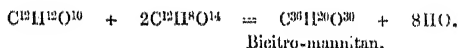


C. By heating mannite with the *terbasic acid*, citric acid, citro- and bicitro-mannitan are formed.

a. From 1 at. mannitan and 1 at. acid, with elimination of 6 at. water:



b. From 1 at. mannitan and 2 at. acid, with elimination of 8 at. water:



Proceeding on the assumption that, in the formation of the true bicitro-mannitan, 4 at. more water must be eliminated, Van Bemmelen regards the last compound as belonging to a distinct class. In this case, however, bisticro-mannitan and various other bodies would have to be excluded from the class of mannitanides. [Kr.]—Berthelot's nomenclature is founded on the assumption that the atom of mannitan is half as great as that here adopted, viz. =  $\text{C}^6\text{H}^6\text{O}^5$ . His *mannite-monobutyric* is accordingly the same as the bibutyro-mannitan of this Handbook, etc.

In the following cases, special phenomena accompany the heating of mannite with organic acids.

a. On heating mannite with excess of *oxalic acid* to 110°, the acid is decomposed into carbonic and formic acids, and an instable compound of formic acid and mannite is produced. (Knop.—See below.) At first, and before the decomposition of the oxalic acid takes place,



mannit-oxalic acid is formed, the lime-salt of which is obtained by neutralising the melted mass with carbonate of lime and precipitating the aqueous solution with alcohol. On heating more strongly, formic and carbonic acids escape, while a mixture of mannit-oxalic acid, mannitan and humous substances remain. (Van Bemmelen.)

$\beta$ . Equal atoms of mannite and *succinic acid* heated to  $140^\circ$  till the melted mass, on cooling, no longer becomes crystalline, but forms a thick syrup, yield a residue which is still soluble in water, and gives, on addition of oxide of lead (succinate of lead separating at the same time), soluble manni-succinate of lead,—an easily decomposable compound, which is precipitated by alcohol and contains varying quantities of lead-oxide, the proportion sometimes corresponding to the formula  $C^{12}H^{12}O^{10}, C^8H^4O^6, PbO$ . This manni-succinic acid differs from succinomannite (see below) only by the quantity of water contained in it, and when more strongly heated is converted into that compound.—When a mixture of 1 at. mannite with 2 at. or more succinic acid is heated, a large quantity of succinic acid sublimes between  $130^\circ$  and  $150^\circ$ , then a large quantity of water is given off, and a hard dry mass is formed, from which succinic acid again sublimes at  $160^\circ$ — $170^\circ$ . The black residue imparts an acid reaction to water, only after standing for some time. It contains more carbon and hydrogen than corresponds to succino-mannitan, hence Van Bemmelen regards it as a mixture of this compound with bisuccino-mannitan. (Van Bemmelen.)

$\gamma$ . A mixture of mannite and citric acid in atomic proportions melts together at  $100^\circ$ , water of crystallisation being given off. At  $130^\circ$ — $140^\circ$  water is again given off, and the mass, which at first is perfectly fluid, becomes pasty without evolution of gas or coloration, and at last hard, dry and tasteless, and is found to be converted into citro-mannitan. At  $170^\circ$ — $180^\circ$  it becomes brown and an oil distils over. In this case also, according to Van Bemmelen, a compound corresponding to manni-succinic acid is formed.—From a mixture of 1 at. mannite and 2 at. citric acid, there is formed at  $140^\circ$ , a neutral, bright yellow substance, the bicitro-mannitan of this Handbook; at  $160^\circ$ — $170^\circ$  it is decomposed and yields, without previously parting with more water, the decomposition-products of citric acid. (Van Bemmelen.)

16. Heated in a sealed tube with aqueous *ammonia*, mannite forms a brown, nitrogenous product, corresponding to that furnished by cane-sugar (p. 260), which smells like horn when heated. (P. Thénard, *Bull. Soc. Chim. Paris*, 1861, 42.)—17. Mannite melted with *potash-hydrate* yields the same product as cane-sugar (p. 260). (Gottlieb. *Ann. Pharm.* 52, 122.) If mannite is thrown into potash-hydrate melted at so low a temperature that only a small quantity of hydrogen is given off, a bulky froth is produced, which does not at once solidify and contains but little oxalic acid. (Leuchtweiss.)—18. By distilling mannite with *lime*, much hydrogen is evolved, and metacetone (ix. 409) and empyreumatic products are obtained. (Favre.)—19. Mannite easily reduces *oxide of silver*. (Favre.) According to Riegel, it reduces aqueous *mercury-*, *silver-*, and *gold-salts*,—20. Aqueous *red prussiate of potash* mixed with  $\frac{1}{2}$  pt. hydrate of potash acts but slightly and slowly on mannite at  $70^\circ$ , but after the mannite has been boiled with acids, it decolorises variable quantities of the mixture. (Gentile, *Dingl.* 158, 127; *Chem. Centr.* 1861, 93.)

Mannite is not altered by ebullition with dilute acids, aqueous alkalis, or potassio-cupric tartate.

21. Mannite is not fermented by contact with yeast (Pelouze and others). It is decomposed by lactous ferment (p. 276), in presence of chalk, with evolution of carbonic acid and water, and formation of alcohol, lactic acid and butyric acid (Pasteur, *N. Ann. Chim. Phys.* 52, 404). Animal membranes produce lactic acid from mannite (Fremy, *Compt. rend.* 9, 165). Fremy is also of opinion that, in the lactous fermentation of sugar, this substance is first converted into mannite and then into lactic acid.—When a mixture of mannite with chalk and *cheese* (gelatin, pancreatic tissue, albumin, or other nitrogenous constituents of the animal body) is left to itself for some weeks at a temperature of 40°, the nitrogenous substance and the mannite are decomposed simultaneously, and with elimination of carbonic acid, nitrogen, hydrogen, alcohol, lactic acid, butyric acid, and acetic acid (Berthelot). This decomposition is independent of access of air, and is not accompanied by the appearance of yeast-cells. The quantity of alcohol obtained amounts to between 13 and 33 p. c. of the decomposed mannite, but no glycerin, fat, or sugar is formed at any stage of the decomposition. Acetic and butyric acids make their appearance as decomposition-products of lactic acid. In presence of carbonate of lime, the reaction becomes irregular, and a peculiar sugar (p. 310) is formed, especially under the influence of testicular tissue. (Berthelot, *N. Ann. Chim. Phys.* 50, 334).

*Combinations.* A. *With Water.* — Mannite exposed to air saturated with moisture takes up only 2 per cent. of water. It dissolves in 6.4 pts. water at 18°, in 6.14 pts. at 20° (Berthelot), in 5 to 6.6 pts. at 16–20° (De Luca) in 4 pts. at 12° (Kircher), in 5 pts. of cold, and in any quantity of hot water (Vogel). Sometimes on shaking up the mannite with water, a larger quantity dissolves, amounting to  $\frac{1}{10}$  of the water; but the solution on standing deposits such a quantity of mannite that the above proportion is attained (Berthelot). When 87.6 grm. mannite are dissolved in 348 grm. water at 16.5° (that is in 4 pts.) the temperature falls to 13.5° (Pohl, *J. pr. Chem.* 82, 155).

B. *With Bases.* — *Potassium-compound.* — When 1 pt. mannite and 1 pt. potash-hydrate are dissolved in 6 pts. warm alcohol of 85 p. c. the liquid on cooling separates into two layers, the lower of which must be washed with hot absolute alcohol and dried at 100°. White, easily friable, strongly alkaline, saline mass, which contains 25 p. c. potash, requires a higher temperature to decompose it than sucrate of potash, and deposits mannite when its alkaline solution is exposed to the air. It is insoluble in absolute alcohol, but dissolves easily in aqueous alcohol (Brendecke).

*Sodium-compound.* — Obtained like the potassium-compound, which it also resembles. Contains 21.6 p. c. soda (Brendecke).

Mannite unites with *chloride of sodium*, forming colourless crystals containing 24.2 p. c. NaCl (Riegel, *Jahrb. pr. Pharm.* 4, 8; *Pharm. Centr.* 1841, 693). Neither Leuchtweiss nor Knop & Schnedermann were able to obtain this compound; Riegel's other statements likewise show that his mannite contained glucose. (Kr.)

*Barium-compound.* — When the solution obtained by triturating together equal pts. of baryta-crystals, water and mannite, is mixed with absolute alcohol, a resinous precipitate is formed, which, after

washing with hot alcohol, contains 23.2 p. c. baryta. It has a strongly alkaline taste. When it is heated in a stream of carbonic acid, mannite separates out. It dissolves in water and in aqueous alcohol but not in absolute alcohol (Brendecke). — When mannite is mixed with an equivalent quantity of baryta-crystals and 3 or 4 pts. water, the mixture left to stand for two days and occasionally shaken, and the filtrate precipitated with alcohol, the flocks which fall down unite to a thick syrup, which may be purified by repeated solution in water and precipitation with alcohol. On heating this syrup in the water-bath, there remains a translucent, very tenacious and glutinous mass, which increases to 4 or 5 times its original volume when heated to  $100^{\circ}$ , and on cooling forms a deliquescent, tumefied, translucent glass. The aqueous solution when left to itself deposits crystals of baryta, solidifies, when heated, to a compact mass like coagulated white of egg, and becomes only partially clear on cooling (Ubal dini).

After drying over oil of vitriol, it contains 15.4 p. c. water, which escapes at  $160^{\circ}$ ; in the anhydrous state, it contains from 37.6 to 37.9 p. c. baryta, and from 63.0 to 62.7 p. c. mannite, corresponding to the formula  $C^{12}H^{14}O^{12}, 2BaO$ . So according to Ubal dini; but his formula just quoted requires 62.73 p. c.  $BaO$  and 37.27 p. c. mannite, whereas his analytical data (perhaps affected with press-errors) give 37.68 and 17.95 p. c.  $BaO$ , 47.00 and 61.93 mannite. The true formula of the compound appears to be  $2C^{12}H^{14}O^{12}, 3BaO + 12H_2O$  (calc. 38.79 p. c.  $BaO$ , 61.21 mannite, 15.43 water). Kr.

*Strontium-compound.* — Aqueous mannite dissolves strontia, the quantity dissolved at the boiling heat being about one-fourth of the weight of the mannite. (Kiegl.) The strontia-salt is obtained like the baryta-compound, which it resembles. The aqueous solution becomes but slightly turbid on boiling. The compound dried at  $100^{\circ}$  gives off from 22 to 24 p. c. water at  $120^{\circ}$ , and then contains from 20.1 to 21.0 p. c. strontia, and 80.0 to 78.5 p. c. mannite, corresponding to the formula  $SrO, C^{12}H^{14}O^{12}$  (calc. 22.15 p. c.  $SrO$  and 77.85 mannite); in the hydrated state, with 8 at. water (calc. 23.54 p. c.). (Ubal dini.)

*Calcium-compound.* — Aqueous mannite dissolves hydrate of lime, with evolution of heat. (Brendecke.) If the solution contains in 100 c. c. 1.6 gr. mannite or less, it takes up constantly 3.7 pts. lime to 100 pts. mannite (after deducting the lime which the water itself would dissolve); but more concentrated solutions take up a larger quantity, those containing 2.4 grms., 4.8 grms. and 9.6 grms. mannite in 100 c. c. taking up respectively 4.5, 4.7 and 6.27 pts. lime to 100 pts. mannite (Berthelot, *N. Ann. Chim. Phys.* 46, 177). The solution has an alkaline taste and reaction, becomes turbid when heated and clear again on cooling (Brendecke). The concentrated solution solidifies when heated to  $85^{\circ}$ , and completely at  $90^{\circ}$ , forming a compact mass containing 50 p. c. lime, therefore perhaps the sexbasic compound  $C^{12}H^{14}O^{12}, 6CaO$ , and becomes quite clear again when cooled to  $50^{\circ}$ . When excluded from the air, it deposits a precipitate, and in contact with the air, yields shining crystals, probably consisting of penta-hydrated carbonate of lime. On addition of hydrochlorate of strontia or magnesia, it yields precipitates, which, after washing, are free from mannite (Ubal dini).

a. *Bibasic.* —  $C^{12}H^{14}O^{12}, 2CaO$ . — A mixture of 200 pts. mannite and 66 pts. hydrate of lime is covered with 600 pts. of water, and left to stand for two days with frequent agitation, and the filtrate is precipitated with alcohol. The white flocks unite into a resinous mass, which is purified

by repeated solution and precipitation out of contact of air. Dried over oil of vitriol between  $100^{\circ}$  and  $120^{\circ}$ , it gives off 14 p. c. water (4 at. = 13.13 p. c.), and at  $160^{\circ}$ , it turns yellow, without further loss. It is decomposed by carbonic acid, without separation of mannitan. After drying at  $120^{\circ}$ , it contains, on the average, 23.45 p. c. lime and 76.65 p. c. mannite (calc. 23.53 p. c. CaO, 76.47 p. c. mannite). (Ubal dini.)

b. *Monobasic compound*.— $C^{12}H^{14}O^{12}, CaO$ . *Bimannitate of Lime*.—When a solution of the bibasic compound is left to evaporate, crystals of mannite first separate out containing 5.3 p. c. lime; and the mother-liquor, on standing, deposits a crystalline salt, which, after drying at  $120^{\circ}$ , contains on the average 13.22 p. c. CaO and 86.15 p. c. mannite, answering to the formula  $C^{12}H^{14}O^{12}, CaO$  (calc. 13.33 p. c. CaO, 86.67 mannite). (Ubal dini.)

Aqueous mannite dissolves *magnesia* and a small quantity of moist *hydrate of alumina* (Riegel).—A solution of mannite heated with potash-ley behaves with *nitrate of cobalt* like cane-sugar (p. 263). (Herzog, *N. Br. Arch.* 50, 299.)

*Lead-compounds*.—Aqueous mannite dissolves lead-oxide, forming an alkaline liquid precipitable by ammonia. It is not precipitated either by neutral or by basic acetate of lead, but an ammoniacal solution of the neutral acetate produces a precipitate in the concentrated solution of mannite (Berthelot).—The mannite may be recovered from the lead-compound in its original state.

a. *Serbasic*.—The compound *b* treated in the recently precipitated state with cold, or after drying, with boiling water, is resolved into an insoluble basic and a soluble neutral lead-compound of mannite.

						Favre. mean.
12 C .....	72.0	...	8.81	.....		8.82
10 H .....	10.0	...	1.22	.....		1.24
8 O .....	64.0	...	7.83	.....		7.91
6 PbO .....	670.8	...	82.14	.....		82.03
<hr/>						
$C^{12}H^{10}Pb^{4}O^{12}, 2PbO$ .....	816.8	...	100.00	.....		100.00

b. *Quadribasic*.—Into a warm ammoniacal solution of neutral acetate of lead, a concentrated aqueous solution of mannite is poured, in quantity not sufficient for complete precipitation. The mixture, which is clear at first, deposits, after standing for some time, slender laminae, which must be collected out of contact with the air and pressed. The same compound is separated from the preceding mixture by alcohol, and may be obtained pure by washing with alcohol.—It does not give off the whole of its water in vacuo till heated to  $130^{\circ}$ , turning yellow at the same time, but without further alteration. It is decomposed by boiling with water, or in the recently precipitated state, even by washing with cold water, the basic compound *a* then remaining. The filtrate yields by evaporation a crystalline deposit of *b*, and if evaporated in vacuo after the removal of this deposit, it leaves a mass which, after drying at  $130^{\circ}$ , contains 67.9 p. c. lead-oxide, together with carbon, hydrogen and oxygen, in proportions answering to the formula  $C^6H^6O^4$ . (Favre.)

at 136° in vacuo.				Favre. mean.
12 C .....	72.0	....	12.16	..... 12.15
10 H .....	10.0	....	1.69	..... 1.67
8 O .....	64.0	....	10.81	..... 10.83
4 PbO .....	447.2	....	75.34	..... 75.30
$C^{12}H^{10}Pb^4O^{12}$ .....				100.00

Knop regards Favre's lead-compounds as mixtures (see *Pharm. Centr.* 1850, 50).

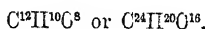
Mannite protects *ferric salts* from precipitation by various reagents (H. Rose). Aqueous mannite does not dissolve the oxides of *antimony*, *bismuth*, *zinc*, *iron* or *tin* (Riegel).

Aqueous mannite does not dissolve *cupric oxide* (Riegel)—From an aqueous solution of mannite mixed with *cupric sulphate*, potash throws down a blue precipitate which dissolves in excess of the alkali, without undergoing any alteration on boiling.

Mannite is nearly insoluble in cold absolute *alcohol*, and but sparingly soluble in the same liquid when heated (Buchholz); in hot aqueous alcohol it dissolves in such quantity that the liquid solidifies to a crystalline pulp on cooling. It dissolves at 14° in 1430 to 1660 pts. absolute alcohol, and at 1.5° in 84 to 90 pts. alcohol of sp. gr. 0.8985 (Berthelot).—Insoluble in *ether*.

#### Appendix to Mannite.

#### Mannide.



BERTHELOT (1856). *N. Ann. Chim. Phys.* 47, 312; *Chim. organ.* Paris 1860, 2, 204; *Lieb. Kopp. Jahresber.* 1856, 657.

Obtained in one instance by heating mannite with butyric acid in a sealed tube to a temperature between 200° and 250°. After decanting the liquid containing the butyric acid, there remained at the bottom of the vessel, crystals of mannite, and a liquid which, when dissolved in water, evaporated to dryness, taken up with absolute alcohol, again evaporated, washed with ether, redissolved in alcohol, and evaporated—yielded mannide.

*Properties.* Thick, scarcely fluid syrup, having a sweet taste, with bitter after-taste. Neutral. Volatilises slightly at 100°, more at 140°. Volatilises when heated on platinum-foil, apparently without decomposition.

at 104°.				Berthelot.
12 C .....	72	....	49.3	..... 48.7
10 H .....	10	....	6.9	..... 7.3
8 O .....	64	....	43.8	..... 44.0
$C^{12}H^{10}O^8$ .....				100.0

Deliquesces in contact with the air, and is partially converted into mannite. In a moderately damp atmosphere, it takes up 40 p. c. water in 12 hours; in an atmosphere saturated with moisture, it takes up 80 per cent. in 4 days, part of the water evaporating again on standing, and crystals of mannite separating out. — When left in contact with *oil of vitriol* at 100° for several hours, it forms a compound whose baryta-salt is amorphous and insoluble in water. When mannide is heated to 200° with *benzoic acid*, a neutral compound insoluble in ether is formed, probably bibenzo-mannite. — When mannide is heated to 100° with *baryta-crystals*, a small portion of it is converted into mannite.

Soluble in *water* and in absolute *alcohol*; insoluble in *ether*.

### Mannitan.



BERTHELOT. *N. Ann. Chim. Phys.* 47, 306; *Lieb. Kopp. Jahresber.* 1856, 655; *Chim. organ.* Paris, 1860, 2, 172.

*Formation.* 1. By heating mannite to 200°. — 2. By decomposing mannitic ethers with water at 240°, with acids, alkalis, or lead-oxide at 100°, or with alcohol. — 3. By heating mannite with concentrated aqueous or alcoholic hydrochloric acid.

*Preparation.* 1. When mannite is heated for some minutes to 200° in an open capsule, part of it gives off water, and is converted into mannitan, while another portion remains undecomposed. The product is dissolved in water; the solution evaporated till the undecomposed mannite crystallises; the last mother-liquor evaporated to dryness over the water-bath; and the residue exhausted with absolute alcohol, which takes up the mannitan. To remove the secondary products formed by the heat, the alcoholic solution is digested for some hours with oxide of lead; the filtrate mixed with water is freed from dissolved lead by sulphuretted hydrogen, and evaporated to dryness; and the mannitan is extracted from the residue by absolute alcohol. — 2. Mannite is boiled with fuming hydrochloric acid in a long-necked flask for 60 hours; the liquid is evaporated over the water-bath; the residue mixed with oxide of lead and digested with alcohol; and the solution, after being treated with sulphuretted hydrogen, and freed from sulphide of lead by filtration, is evaporated to dryness. The residual syrup is treated with absolute alcohol; any mannite that may remain mixed with it is suffered to crystallise out; the filtrate is evaporated; and the mannitan which remains is further purified by washing with ether, re-solution in absolute alcohol, and evaporation. — 3. Mannite may also be dissolved in a mixture of alcohol and fuming hydrochloric acid, and the solution heated to 100° in a sealed tube for 60 hours, the liquid then separating into two layers, the upper of which consists of chloride of ethyl. This is removed, the lower aqueous stratum evaporated to dryness over the water-bath, and the residue purified as in (2). — 4. When stearo-mannite is heated with water in a sealed tube to 240°, stearic acid separates, and an aqueous

Appears to be produced under the same circumstances as mannito-bisulphuric acid (p. 371), and known, like that compound, only in combination with water and with bases. Discovered by Knop & Schnedermann. More recently (*Pharm. Centr.* 1849, 803, and 1850, 51), the former expresses a doubt as to whether the substances examined by themselves and by Favre were of definite chemical constitution.

The lead-salt is obtained in aqueous solution by dissolving mannite in oil of vitriol, diluting with water, digesting with carbonate of lead, and filtering from sulphate of lead; and this solution, decomposed by hydrosulphuric acid, yields aqueous mannito-ter sulphuric acid, as a colourless strongly acid liquid, which is resolved by evaporation into mannite and sulphuric acid.

The mannito-ter sulphates are easily decomposable, and are all soluble in water. Knop & Schnedermann gave the formula  $C^8H^7M^2O^3, 4SO^3$ ; Gerhardt (*Compt. chim.* 1, 20) and Strecker, that which is here adopted.

*Potash-salt.*—Obtained as a yellow syrup by precipitating the aqueous lead- or baryta-salt with sulphate of potash, and evaporating the filtrate at a gentle heat. This syrup dries up between  $50^\circ$  and  $60^\circ$  to a translucent deliquescent gum, which is insoluble in alcohol and contains a small quantity of sulphate.

Knop & Schnedermann.					
12 C .....	72.0	....	13.42	.....	14.13
11 H .....	11.0	....	2.05	.....	2.40
6 S .....	96.0	....	17.89	.....	17.45
27 O .....	216.0	....	40.25	.....	40.04
3 KO .....	141.6	....	26.39	.....	25.98
<hr/>					
$C^{12}H^{11}K^3O^{12}, 6SO^3$ .....	536.6	....	100.00	.....	100.00

*Soda-salt.*—Obtained like the potash-salt, which it also resembles.

Knop & Schnedermann.					
12 C .....	72	.....	14.75	.....	14.48
11 H .....	11	.....	2.25	.....	2.47
6 S .....	96	.....	19.67	.....	
27 O .....	216	.....	44.27	.....	
3 NaO .....	93	.....	19.06	.....	18.84
<hr/>					
$C^{12}H^{11}Na^3O^{12}, 6SO^3$ .....	488	....	100.00	.....	

*Baryta-salt.*—A solution of mannite in oil of vitriol is mixed with water, and the solution is neutralised with carbonate of baryta and evaporated, during which process small quantities of sulphate of baryta are continually deposited. The solution, concentrated till it forms a saline crust, deposits, on cooling, white crystalline grains, and if somewhat more concentrated, solidifies to a jelly, which dries up to a white fissured mass. Alcohol precipitates it from the aqueous solution as a white, indistinctly granulo-crystalline powder. The salt is easily decomposed by heat. — More recently Knop makes the following statements:—The baryta-salt, prepared as above, by evaporating the solution and drying at  $65^\circ$ , gave 45.5 p. c.  $BaO, SO^3$ ; the same solution, precipitated with absolute alcohol, yielded a salt which gave 49.7 p. c.  $BaO, SO^3$ , 14.56 C. and 2.4 N. The solution remaining after this precipitation, left, on evaporation to dryness, a salt which gave 25.8 p. c.  $BaO, SO^3$ . Hence, Knop regards it as probable that the salts examined by himself and Schnedermann were mixtures (*Pharm. Centr.* 1849, 802).

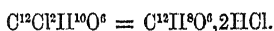
Knop & Schnedermann.					
12 C .....	72.0	....	11.53	.....	11.19
11 H .....	11.0	....	1.76	.....	2.03
6 S .....	96.0	....	15.37	.....	15.32
27 O .....	216.0	....	34.59	.....	35.11
3 BaO .....	229.5	....	36.75	.....	36.35
<hr/>					
$C^{12}H^{11}Ba^3O^{12}, 6SO^3$ ....	624.5	....	100.00	.....	100.00

37.97 p. c. BaO corresponds to 57.82 p. c.  $BaO, SO^3$ .

*Lead-salt.* — (Preparation p. 372.) The aqueous solution deposits sulphate of lead when evaporated at a gentle heat, and leaves a turpentine-like mass which decomposes on further exposure to heat. Precipitated by alcohol from the concentrated solution in oil-drops, which dry up, in vacuo, to a yellow amorphous deliquescent mass, and leave a small quantity of sulphate of lead when dissolved in water.

Knop & Schnedermann.					
12 C .....	72.0	....	9.87	.....	9.48
11 H .....	11.0	....	1.41	.....	
6 S .....	96.0	....	13.26	.....	
27 O .....	216.0	....	29.62	.....	
3 PbO .....	334.2	....	45.84	.....	44.38
<hr/>					
$C^{12}H^{11}Pb^3O^{12}, 6SO^3$ ....	729.2	....	100.00	.....	

### Chlorhydro-mannitan.



BERTHELOT. *N. Ann. Chim. Phys.* 47, 334; *Chim. organ.* 2, 197; *Lieb. Kopp. Jahresber.* 1856, 661.

*Mannite chlorhydrique or monochlorhydrique ; Chlormannitanafer* (p. 362).

Mannite is heated to 100° in a closed tube with 10 to 15 pts. fuming hydrochloric acid; the liquid is neutralised with carbonate of potash, shaken up with ether, and evaporated; the syrup is left at rest for some months in vacuo; and the crystals which separate are purified by recrystallisation from ether. There remains a mother-liquor, perhaps consisting of similar compounds.

White, microscopic crystals resembling mannite, with a bitter aromatic taste and aromatic odour, which is emitted when they are heated. Neutral. Melts when heated, and solidifies in a crystalline mass on cooling. Volatilises without decomposition when heated on platinum-foil.

Berthelot.					
12 C.....	72	....	35.82	.....	35.9
2 Cl .....	71	....	35.32	.....	
10 H .....	10	....	4.97	.....	5.6
6 O .....	48	....	23.89	.....	
<hr/>					
$C^{12}Cl^2H^{10}O^6$ .....	201	....	100.00	.....	

The vapour, when set on fire, burns with a green-edged flame, and



forms hydrochloric acid.--Decomposed by lime into mannitan and hydrochlorate of lime. Not precipitated by *nitrate of silver* from the alcoholic solution.

Soluble in *alcohol* and in *ether*.

### Compound of Formic Acid with Mannite.

W. KNOP. *J. pr. Chem.* 48, 362; abstr. *Ann. Pharm.* 74, 347; *Pharm. Centr.* 1849, 303.

*Formite. Ameisensäure-Mannit* (see page 363).

Formed by heating mannite with excess of oxalic acid, which is thereby resolved into formic and carbonic acids. The mixture is heated for five hours to  $110^{\circ}$ , then for a few hours to  $96^{\circ}$ , to expel excess of formic acid and carbonic acid, after which there remains a colourless syrup which is liquid while hot, and solidifies on cooling. From this product, the last traces of formic acid may be removed by ether.

When left for some time over oil of vitriol, it becomes turbid and acquires an odour. In contact with *bases*, it is quickly resolved into 1 at. mannite and 2 at. formate, and is therefore, perhaps,  $C^{12}H^{10}O^8, 2(C^2H^2O^4)$  (Knop). Later (*Chemische Methoden*, Leipzig, 1859, 281), Knop gives the formula  $C^{12}H^{14}O^{12}, C^2H^2O^4$ , which does not agree with his earlier analysis. He regards it as doubtful whether this compound belongs to the ethers of the third class (*Ester*, vii, 215), inasmuch as it is much less stable than Berthelot's mannitic ethers.

### Ethylo-mannitan.



BERTHELOT. *N. Ann. Chim. Phys.* 47, 341; *Chim. organ.* 2, 203; *Lieb. Kopp. Jahresber.* 1856, 663.

*Mannitanvinifer.*

A mixture of mannite, potash-hydrate, a small quantity of water, and bromide of ethyl, is heated to  $100^{\circ}$  in a sealed tube for 30 or 40 hours, then shaken up with ether and the extract evaporated.

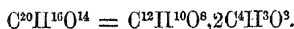
Colourless, bitter syrup, which volatilises without decomposition when heated on platinum-foil.

						Berthelot.
20 C	.....	120	....	54.54	.....	51.3
20 H	.....	20	....	9.09	.....	9.7
10 O	.....	80	....	36.37	.....	36.0
<hr/>						
$C^{20}H^{20}O^{10}$	....	220	....	100.00	.....	100.0

Carbonises when heated in a tube. — Decomposed by a mixture of *oil of vitriol* and butyric acid, with formation of butyrate of ethyl.

Nearly insoluble in water, easily soluble in *alcohol* and *ether*.

## Aceto-mannitan.



BERTHELOT. *N. Ann. Chim. Phys.* 47, 315; *Chim. organ.* 2, 185; *Lieb. Kopp. Jahresber.* 1856, 657.

*Mannite acétique* or *monoacétique*. — *Biessigsäure-Mannitanäther*, *Essigmannitanester*.

*Formation*. By heating mannite with glacial acetic acid to 200°—220°. In contact with oil of vitriol and acetic acid, at mean temperatures, or with glacial acetic acid at 100° C., mannite forms only traces of this compound.

*Preparation*. A mixture of glacial acetic acid and mannite is heated to 200°—220° for 50 or 60 hours; and the product is mixed with aqueous soda-solution, neutralised completely by adding a small quantity of solid potash, and shaken up with ether as long as that liquid takes up any of the compound. The ethereal extracts are decolorised with animal charcoal and evaporated in vacuo at a gentle heat.

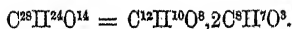
*Properties*. Neutral syrup, having a very bitter taste. Inodorous in the cold, but gives off a peculiar odour when gently heated. When heated on platinum-foil it volatilises almost without decomposition. — Decomposed with baryta-water, it yields 46·4 p. c. acetic acid (calc. 48·4 p. c.  $\text{C}^4\text{H}^4\text{O}^4$ ), and 74·4 p. c. mannite, together with mannitan (calc. 73·7 p. c. mannite).

Berthelot,					
20 C	.....	120	...	48·39	..... 48·7
10 H	.....	16	...	6·45	..... 6·7
14 O	.....	112	...	45·16	..... 44·6
<hr/>					
$\text{C}^{20}\text{H}^{16}\text{O}^{14}$	.....	248	...	100·00	..... 100·0

*Decompositions*. 1. *Heated* in a tube, it decomposes and gives off an odour of caramel. — 2. It undergoes but very slight alteration when kept for many months in contact with *water* containing alcohol. — 3. *Alcoholic hydrochloric acid* decomposes it in a few days, into mannitan and acetic acid; but by longer-continued action, mannite is likewise formed. — 4. *Baryta-water* acts slowly at 100°, decomposing it completely in 50 hours, into mannitan and acetate of baryta.

In *water* it dissolves without decomposition, even at the boiling heat. Soluble in *alcohol* and in *ether*, but not in *sulphide of carbon*.

## Bibutyro-mannitan.



BERTHELOT. *N. Ann. Chim. Phys.* 47, 319; *Chim. organ.* 2, 188; *Lieb. Kopp. Jahresber.* 1856, 658.

*Mannite monobutyrique* (Berthelot). *Bibuttersäure-mannitanester*.

Obtained, in larger quantity than aceto-mannite, by heating mannite with butyric acid to  $200^{\circ}$  for ten hours, and purified in the same manner as aceto-mannite.

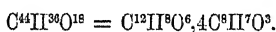
Semifluid, tenacious mass, intermixed with microscopic needles, mobile and having a faint odour when hot. Neutral. Tastes very bitter. When heated on platinum-foil, it volatilises in thick vapours and almost without decomposition. Decomposed by baryta-water, it yields 60.4 p. c. butyric acid and 52.2 p. c. mannitan (calc. 57.9 p. c.  $C^8O^4$  and 54.0  $C^{12}H^{12}O^{10}$ .)

					Berthelot.
					mean.
28 C .....	168	....	55.26	.....	54.85
24 H .....	24	....	7.89	.....	7.85
14 O ....	112	....	36.85	.....	37.30
<hr/>					
$C^{28}H^{24}O^{14}$ .....	304	....	100.00	.....	100.00

*Decompositions.* 1. When the compound is rapidly heated, a small portion of it chars, burns with a white luminous flame, and an odour like that emitted by tartaric acid under similar circumstances. — 2. By contact for some months with water containing alcohol, or by boiling for several hours, a small portion of the acid is set free. Complete decomposition into butyric acid and mannitan is effected by heating it with water to  $240^{\circ}$ . — 3. Alcoholic hydrochloric acid, even in the cold, forms mannitan and butyric ether. — 4. The compound is likewise decomposed into mannitan and a butyrate by heating with baryta-water or lead-oxide. — By excess of butyric acid at  $200^{\circ}$ — $250^{\circ}$ , it is converted into quadributyro-mannitan.

Insoluble in water, slightly soluble in sulphide of carbon, easily in alcohol and ether.

### Quadributyro-mannitan.



BERTHELOT, *loc. cit.*

*Mannite dibutyrique. Quadributtersäure-mannitanester* (p. 362).

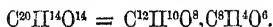
Obtained by heating bibutyro-mannitan with excess of butyric acid to  $200^{\circ}$ — $250^{\circ}$ , and purified like aceto-mannite.—When a mixture of equal pts. mannite, butyric acid and oil of vitriol is left to itself for a week, then diluted with water, neutralised with carbonate of potash, and shaken up with ether, the ether takes up an oil which contains 58.3 carbon and 7.8 hydrogen, but yields on decomposition a small quantity of sulphuric acid as well as butyric acid and mannitan.

Colourless, bitter, neutral oil, which volatilises without residue when heated on platinum foil.

				In vacuo.	Berthelot.
44 C .....	264	....	59.47	.....	59.8
36 H .....	36	....	8.11	.....	8.2
18 O .....	144	....	32.42	.....	32.0
<hr/>					
$C^{44}H^{36}O^{18}$ .....	444	....	100.00	.....	100.0

Soluble in alcohol and precipitated by water.

## Succino-mannitan.



VAN BEMMELN. *Scheikund. Verhandelingen en Onderzoek.* 13; abstr. *Kopp's Jahresber.* 1858, 434.

*Bernsteinsäure-mannitanester* (p. 363).

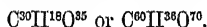
Mannite and succinic acid in equal numbers of atoms are heated together in the oil-bath to 170°, whereupon the mixture gives off water and melts to a yellow liquid, and then solidifies to a hard, dark-grey mass, which is to be triturated and well boiled with alcohol. Tasteless. Neutral.

at 170°—180°.				van Bemmelen.
				mean.
20 C .....	120	....	48.73	..... 48.90
14 H .....	14	....	5.68	..... 5.53
14 O .....	112	....	45.54	..... 45.57
<hr/>				<hr/>
$C^{20}H^{14}O^{14}$ .....	246	....	100.00	

Decomposed by prolonged boiling with *water*. — Dissolves in *oil of vitriol* and in warm *nitric acid*, succinic acid being set free, and mannite entering into combination with the mineral acid. — Decomposed by boiling with lead-oxide, with separation of succinate of lead, part of the lead, however, remaining in solution as mannito-succinate.

Insoluble in *water*, *alcohol*, and *ether*.

## Mannitartaric Acid.



BERTHELOT. *N. Ann. Chim. Phys.* 47, 330; *Chim. organ.* 2, 200; *Lieb. Kopp. Jahresber.* 1856, 660.

*Acide mannitartrique* or *mannitritartrique*, *Mannitartersäure*. — Known only in combination (p. 363).

When a mixture of equal pts. mannite and tartaric acid is heated for five hours to 100° — 120° in a open vessel, a glutinous very acid mass is produced, which is a mixture of mannitartaric acid, tartaric acid and mannite. This mixture is triturated with carbonate of lime and a small quantity of water till it becomes neutral, then filtered and precipitated with alcohol. The precipitated mannitartarate of lime purified by repeated solution in water and precipitation with alcohol, and decomposed in aqueous solution with an equivalent quantity of oxalic acid, yields aqueous mannitartaric acid, which is gradually resolved into mannite and tartaric acid.

Mannitartaric acid is terbasic. (Berthelot) If 1 at. of the acid be supposed to contain 1 at. mannite ( $C^{12}$ ), the acid must be regarded as sexbasic, and represented by

the formula  $C^{60}H^{36}O^{70}$  (Kr.) Its salts heated with hydrate of lime to  $100^{\circ}$  for fifty or sixty hours, are resolved into mannite, mannitan, and tartaric acid.

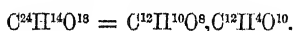
*Mannitartrate of Lime.*—*Terbasic.*—White, loosely coherent, amorphous powder, which dissolves easily in water when recently precipitated, but with difficulty after drying, and is precipitated by alcohol. After drying in vacuo, it retains 6 at. water, 4 at. of which, amounting to 6.0 p. c. (calc. 6.1 p. c.  $H_2O$ ) go off at  $140^{\circ}$ .

	<i>In vacuo.</i>		Berthelot.	
30 C .....	180	....	30.56	..... 30.1
21 H .....	21	....	3.57	..... 3.9
38 O .....	304	....	51.61	..... 52.4
3 CaO .....	84	....	14.26	..... 13.6
<hr/>				
$C^{30}Ca^3H^{15}O^{35}, 6H_2O$ .....	589	....	100.00	..... 100.0

*Mannitartrate of Magnesia.*—Obtained like the lime-salt, *magnesia alba* being used instead of carbonate of lime. On mixing the aqueous solution with alcohol, the salt is precipitated as a soft, semi-fluid mass. It is more soluble than the lime-salt in aqueous alcohol. The salt, after drying in vacuo, gives off 31.2 p. c. water, corresponding to 30 at. (calc. 31.36 p. c.) at  $140^{\circ}$ .

	<i>In vacuo.</i>		Berthelot.	
30 C .....	180	....	20.91	..... 20.7
45 H .....	45	....	5.23	..... 5.1
62 O .....	496	....	57.60	..... 57.5
7 MgO .....	140	....	16.26	..... 16.7
<hr/>				
$C^{30}Mg^3H^{15}O^{35}, 4MgO, 30aq.$ ....	861	....	100.00	..... 100.0

### Citro-mannitan.



VAN BEMMELEN. *Scheikund. Verhandlingen en Onderzoekingen*, 2 Deel, 1 Stuck, Rotterdam, 1858. Onderz. 17; abstr. *Kopp's Jahresber.* 1858, 431.

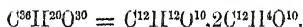
*Citromannitanester* (p. 363).

A mixture of citric acid and mannite in equal numbers of atoms is heated to  $130^{\circ}$  —  $140^{\circ}$ , till the mass becomes dry, friable and tasteless.

Light-yellow, very hygroscopic mass, which decomposes like succinomannitan when boiled with *water*, *alcohol* or *alkalis*, or when *oil of vitriol* or *nitric acid* is poured upon it. — Insoluble in *water*, *alcohol*, and *ether*.

	<i>at 152^{\circ}.</i>		van Bemmelen. <i>mean.</i>	
24 C .....	144	....	47.68	..... 47.12
14 H .....	14	....	4.63	..... 4.83
18 O .....	144	....	47.69	..... 48.05
<hr/>				
$C^{24}H^{14}O^{18}$ .....	302	....	100.00	..... 100.00

## Bicitro-mannitan.

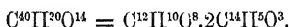


VAN BEMMELER, *loc. cit.*

See pp. 362, 363. — 1 at. mannite is heated to 140° with 2 at. citric acid, till the mass has become hard, dry and tasteless. — Light yellow, neutral mass, decomposed by boiling for some time with *water* or *baryta-water*.

				van Bemmeler.	
				<i>mean.</i>	
36 C .....	216	...	45.38	.....	45.46
20 H .....	20	...	4.20	.....	4.46
30 O .....	240	...	50.42	.....	50.08
<hr/>				<hr/>	
C <sup>36</sup> H <sup>20</sup> O <sup>30</sup> .....	476	...	100.00	.....	100.00

## Bibenzo-mannitan.



BERTHELOT. *N. Ann. Chim. Phys.* 47, 327; *Chim. organ* 2, 193; *Lieb. Kopp. Jahresber.* 1856, 660.

*Mannite benzoïque* or *monobenzoïque*. *Bibenzoemannitanester* (p. 362).

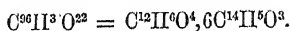
Obtained by heating mannite with benzoic acid to 200° for ten hours, and purified like aceto-mannite (p. 375), till it reacts neutral.

Tough, semi-solid resin which may be drawn out into threads. Neutral, tasteless at first, afterwards bitter and aromatic.

				at 120°.		Berthelot.	
40 C .....	240	...	64.52	.....	64.1		
20 H .....	20	...	5.37	.....	5.8		
14 O .....	112	...	30.11	.....	30.1		
<hr/>				<hr/>		<hr/>	
C <sup>40</sup> H <sup>20</sup> O <sup>14</sup> .....	372	...	100.00	.....	100.0		

When *heated* on platinum-foil, it smells like roasted apples, chars, and burns away without residue. Heated in a test-tube, it yields needles of benzoic acid. — When left for several months in contact with *water* containing alcohol, it turns sour and gives off the odour of benzoic ether. — By alcoholic *hydrochloric acid*, *baryta-water*, and *lead-oxide*, it is decomposed less easily than bibutyro-mannitan. — By a larger excess of *benzoic acid* between 200° and 250°, it is slowly converted into hexabenzo-mannitan.

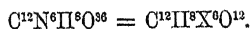
Insoluble in *water*, nearly insoluble in *sulphide of carbon*, easily soluble in *alcohol* and in *ether*.

**Hexabenzomannitan.**

BERTHELOT, *loc. cit.*

*Mannite tribenzoïque; Hexabenzomannitanester.* — Bibenzo-mannitan is heated to  $200^{\circ}$ — $250^{\circ}$  in a sealed tube for 20 hours, with a large excess of benzoic acid; the neutral compound thus formed is extracted from the product, and treated in like manner with benzoic acid a second time; and the product is purified like aceto-mannite.

Solid, neutral resin, which is decomposed by heating with hydrate of lime, and contains 73.4 carbon, 5.2 hydrogen and 21.4 oxygen, corresponding to the formula  $C^{96}H^3O^{22}$  (calc. 73.1 p. c. C., 4.6 H. and 22.3 O.)

**Nitro-mannite.**

FL. DOMONTE & MÉNARD. *Compt. rend.* 24, 89 and 391; *N. J. Pharm.* 12, 159; *Pharm. Centr.* 1847, 892.

SOBRERO. *Compt. rend.* 25, 121; *Ann. Pharm.* 64, 397; *Dingl.* 105, 378.

A. STRECKER. *Ann. Pharm.* 73, 59.

A. KNOP. *Pharm. Centr.* 1849, 806; 1850, 49; *J. pr. Chem.* 48, 369; 49, 228; *Ann. Pharm.* 74, 347.

A. & W. KNOP. *Pharm. Centr.* 1852, 129; in detail: *J. pr. Chem.* 56, 337.

*Mannite quintinitrique* (Domonte & Ménard), *trinitrique* (Berthelot).

*Preparation.* 1 pt. of pulverised mannite is triturated with a small quantity of nitric acid of sp. gr. 1.5 till it dissolves; a small quantity of oil of vitriol is added, then nitric acid and oil of vitriol alternately till  $4\frac{1}{2}$  pts. nitric acid and  $10\frac{1}{2}$  pts. oil of vitriol have been consumed. The pasty mass is mixed with a large quantity of water; and the separated nitromannite is collected, and purified by recrystallisation from alcohol. (Strecker, Knop.) In the mother-liquid there remains a small quantity of a much more fusible product, which may be extracted by ether after neutralisation with carbonate of potash. (Berthelot.)

*Properties.* White, silky needles, melting between  $68^{\circ}$  and  $72^{\circ}$  (Béchamp, *Compt. rend.* 51, 258).

		Domonte & Ménard.		Svanberg & Staaf.		Strecker.	
12 C	72	15.93	17.20	19.40	16.07		
6 N	84	18.58	17.25		18.20		
8 H	8	1.77	1.85	2.15	1.94		
36 O	288	63.72	63.70		63.79		
$C^{12}H^8O^{12}$		452	100.00	100.00		100.00	

Earlier formulæ, the incorrectness of which has been shown by Strecker (—for the sake of uniformity, the nitrogen is given in all cases as hyponitric acid—):  $C^{12}H^7X^5O^{12}$  (Domonte & Ménard);  $C^{12}H^9X^4O^{13}$  (Svanberg & Staaf, *Berz. Jahresber.* 1849, 360);  $C^{12}H^9X^5O^{12}$  (Stenhouse, *Ann. Pharm.* 70, 218). Svanberg & Staaf's analyses led Berthelot (*Chim. organ.* 2, 195) to regard the product examined by them as *Mannite dinitrique*  $C^6H^4X^2O^5$  ( $=C^{12}H^8X^4O^{10}$ ), for which, however, according to Strecker's investigation, there is no real ground, even if (as in the case of dulcite) later experiments should reveal the existence of two nitro-compounds. (Kr.)—According to Knop and others, nitro-mannite contains nitric acid as a proximate constituent, a view of its constitution resting on arguments similar to those adduced in the case of pyroxylin (p. 174).

*Decompositions.* 1. Nitro-mannite, when kept for some years, undergoes a *spontaneous decomposition* attended with evolution of red vapours and of nitric acid (Strecker). See the corresponding decomposition of nitro-dulcite.—2. When heated to  $90^\circ$ , it regularly gives off red vapours and leaves a hard, white, friable residue (Béchamp, *Compt. rend.* 41, 258). When carefully heated in a test-tube, it melts, with slight evolution of red vapours, and solidifies in the crystalline form on cooling. When less strongly heated, it detonates, with abundant evolution of red vapours, and leaves no residue (Strecker).—3. It does not explode by slight friction, but when struck with a hammer, it detonates violently without apparent emission of red vapours, and sets fire to gunpowder mixed with it (Sobrero).—4. *Oil of vitriol* dissolves nitro-mannite abundantly and without evolution of gas; even the addition of copper-turnings produces no alteration; but a few drops of water eliminate large quantities of red vapour, whilst the solution takes up copper and becomes green (Strecker).—*Oil of vitriol* diluted with from 2 to 4 per cent. of water eliminates from nitro-mannite, after some time, colourless vapours of nitric acid (Knop).—5. When an alcoholic solution of nitro-mannite is mixed with a large excess of *sulphide of ammonium* which is completely saturated with hydrosulphuric acid, it is reduced to mannite, with evolution of a large quantity of ammonia and separation of sulphur. If sulphide of ammonium less completely saturated with sulphuretted hydrogen be used, there remains, on evaporation, a coloured product, containing, in addition to mannite, the ammonia salt of an organic acid (Dessaignes, *Compt. rend.* 33, 462); see also Knop, *Pharm. Centr.* 1849, 807.—6. By continued boiling with aqueous *bisulphite of ammonia* completely saturated with sulphurous acid, nitro-mannite is reduced to mannite, with formation of sulphate, nitrite and nitrate of ammonia (A. & W. Knop). Sulphurous acid and hydrosulphuric acid do not appear to act on nitro-mannite.—7. By *ferrous acetate* it is reduced to mannite (Béchamp, *N. Ann. Chim. Phys.* 46, 354), for the most part to mannitan (Berthelot). By treating nitro-mannite with hydrochloric acid and iron, copper or zinc, mannite and many decomposition-products are obtained.

8. By boiling aqueous or cold alcoholic *potash*, nitro-mannite is dissolved, with red brown coloration. (Strecker.)—9. Nitro-mannite heated with *baryta-water* to  $100^\circ$  for forty hours, is dissolved with yellow colour, but neither mannite or mannitan can be detected in the solution (Berthelot, *N. Ann. Chim. Phys.* 47, 340).

Nitro-mannite dissolves in *alcohol* and in *ether*, especially with aid of heat.



*Second Appendix to Mannite.***Mannitic Acid.**

GORUP-BESANEZ. *Ann. Pharm.* 118, 257.

The formation of a non-volatile acid from mannite was first observed by Dübeneiner (*J. pr. Chem.* 28, 498, and 29, 452). — This acid is produced from mannite under the influence of platinum-black (p. 360); perhaps, also, with the aid of nitric acid (p. 360).

*Preparation.* A mixture of 1 pt. mannite and 2 pts. platinum-black is moistened with water and left to itself at a temperature not exceeding  $30^{\circ}$  or  $40^{\circ}$ , the water which evaporates being frequently renewed, till the whole of the mannite is decomposed, which, if 20 or 30 grms. of mannite are used, takes place in about three weeks. If the temperature rises above  $40^{\circ}$ , the acid undergoes further alteration, and if the mixture becomes dry, it sometimes takes fire. — The mass is exhausted with water; the solution is precipitated with basic acetate of lead; and the precipitate is collected, washed, and decomposed by hydrosulphuric acid. The solution filtered from sulphide of lead is evaporated, first over the water-bath, then, when it begins to show colour, in vacuo over oil of vitriol.

*Properties.* Gummy, amorphous mass, without any sign of crystallisation. Tastes purely and strongly acid.

*Decompositions.* 1. When heated to  $80^{\circ}$ , it turns brown, then black, and gives off gas. — 2. Heated on platinum-foil, it takes fire and burns with a luminous flame and an odour of caramel, leaving charcoal. — 3. Its aqueous solution turns brown when heated. — 4. Aqueous mannitic acid heated with cupric-oxide and potash throws down cuprous oxide; from nitrate of silver it precipitates the metal.

*Combinations.* Mannitic acid dissolves in water in all proportions. The concentrated solution does not yield crystals when shaken up with *alkaline bisulphites*.

*With Bases.* Aqueous mannitic acid decomposes carbonates with effervescence, and dissolves zinc and iron, with evolution of hydrogen. The *basic mannitates*  $C^{12}H^{10}M^2O^{14}$  are all, excepting the lead and silver salts, easily soluble in water, and most of them are amorphous or granulo-crystalline. They are insoluble in alcohol, and when precipitated thereby, dissolve with difficulty in water after drying, and in boiling water, they knead together to resinous masses, with partial decomposition. They decompose with great facility.

Mannitic acid likewise forms *basic salts*; *mono-acid salts* Gorup-Besanez did not succeed in preparing. The aqueous acid is not precipitated by the salts of calcium, magnesium, aluminium, zinc, cadmium, copper, silver, or mercury.

*Mannitate of Potash.* — Mannitic acid exactly neutralised with

aqueous potash, becomes turbid on addition of alcohol of about 90 per cent., and deposits a brownish semi-fluid mass, perhaps bibasic mannitate of potash. The solution half neutralised or completely neutralised with potash-ley, turns brown and decomposes when left to itself or evaporated over the water-bath, but does not yield crystals.

*Mannitate of Baryta.* — Aqueous mannitic acid is precipitated by excess of baryta-water. The clear solution of mannitic acid neutralised with baryta-water turns acid from decomposition every time it is evaporated over the water-bath. Mannitate of baryta contains less baryta than is required by the formula of the bibasic salt.

*Mannitate of Lime.* — Lime-water reacts with mannitic acid in the same manner as baryta-water. Aqueous mannitic acid is heated with carbonate of lime till the solution becomes neutral and no longer effervesces; the cooled filtrate is mixed with 2 vol. alcohol of sp. gr. 0·82; the flocks which fall down are collected, washed with alcohol, and redissolved in water; and the solution is reprecipitated with alcohol. — White, earthy powder, — or if the precipitate has been heated under alcohol, — round microscopic granules, without distinct crystalline form, which give off adhering water at 100°. — After drying it is but partially soluble in water, and melts when boiled therewith to a brown resin, brittle when cold.

<i>Dried.</i>				Gorup-Besanez. <i>mean.</i>	
12 C .....	72	....	30·76	.....	30·33
10 H .....	10	....	4·28	.....	4·39
2 Ca .....	40	....	17·09	.....	16·69
14 O .....	112	....	47·87	.....	48·59
$C^{12}H^{10}Ca^2O^{14}$ .....				234	.... 100·00
				.....	100·00

*Mannitate of Lead.* — Acetate and nitrate of lead throw down from aqueous mannitic acid, precipitates containing from 54·82 to 67·8 p. c. lead-oxide, while part of the mannitic acid remains in solution. Basic acetate of lead precipitates mannitic acid completely.

*Bibasic.* — Aqueous mannitic acid is boiled with oxide of lead and filtered hot, the filtrate then depositing a granulo-crystalline precipitate, while part of the salt remains undissolved as resin, and suffers partial decomposition. — When boiled with water, it is converted into a soft resin, brittle when cold.

				Gorup-Besanez. <i>mean.</i>	
12 C .....	72·0	....	17·93	.....	17·64
10 H .....	10·0	....	2·49	.....	2·37
2 Pb .....	207·4	....	51·66	.....	51·45
14 O .....	112·0	....	27·92	.....	28·54
$C^{12}H^{10}Pb^2O^{14}$ .....				401·4	.... 100·00
				.....	100·00

Aqueous mannitic acid partly prevents the precipitation of iron-salts by reagents.

*Cupric mannitate.* — Ammoniacal cupric salts form a green precipitate with aqueous mannitic acid. The aqueous acid, boiled with

hydrated cupric oxide, dissolves only a small quantity, but reduces a portion. From a mixture of the aqueous acid with cupric acetate, alcohol throws down a blue-green precipitate, containing more cupric oxide than the bibasic salt.

*Bibasic.* — Aqueous mannitic acid is heated with green bibasic carbonate of copper (v. 414; if the blue carbonate is used, reduction is apt to take place), and the emerald-green solution is evaporated in vacuo over oil of vitriol. A salt which sometimes separates from the green solution during cooling, usually contains a larger proportion of cupric oxide than the bibasic salt. Shining, green, friable plates, permanent at  $100^{\circ}$ .

	at $100^{\circ}$ .		Gorup-Besanez.	
12 C .....	72.0	....	27.97	..... 27.29
10 H .....	10.0	....	3.88	..... 4.09
2 Cu .....	63.4	....	24.63	..... 24.73
14 O .....	112.0	....	43.52	..... 43.89
$C^{12}H^{10}Cu^2O^{14}$ .....	257.4	....	100.00	..... 100.00

*Mercurous salts* and ammonia throw down from aqueous mannitic acid a white precipitate, which gradually turns grey.

*Mannitate of Silver.* — A strong aqueous solution of mannitate of lime, mixed with a syrupy solution of nitrate of silver, solidifies to a white pulp, which must be washed with cold water. Light olive-green, or greenish yellow powder. When heated in the liquid from which it has been precipitated, it decomposes completely, with separation of metallic silver.

			Gorup-Besanez.	
			mean.	
12 C .....	72	....	17.56	..... 17.52
10 H .....	10	....	2.43	..... 2.19
2 Ag .....	216	....	52.68	..... 52.65
14 O .....	112	....	27.33	..... 27.64
$C^{12}H^{10}Ag^2O^{14}$ ....	410	....	100.00	..... 100.00

Mannitic acid dissolves in *alcohol* in all proportions, but is nearly insoluble in *ether*.

## Dulcite.



LAURENT. *Compt. rend.* 30, 41; *Compt. chim.* 1850, 364; *Ann. Pharm.* 76, 358; *J. pr. Chem.* 49, 403; *Pharm. Centr.* 1850, 217. — *Compt. rend.* 31, 694; *Compt. chim.* 1851, 29; *Ann. Pharm.* 80, 345; *J. pr. Chem.* 53, 170.

JACQUELAIN. *Compt. rend.* 31, 625; *Compt. chim.* 1851, 21; abstr. *Ann. Pharm.* 80, 345; *J. pr. Chem.* 51, 163.

*Dulcose* (Laurent); *Dulcine* (Jacquelin). Found in tubers, of unknown origin, which were sent in large quantity from Madagascar to Paris in 1848, and is extracted therefrom by boiling water. The aqueous

extract, on cooling, yields crystals of dulcite, while a colourless, uncrystallisable syrup remains (Laurent).

*Properties.* Colourless, highly lustrous prisms of the oblique prismatic system, *Fig.* 67 without *t*, but with *m* from *Fig.* 69. Rhombic prism *u* having its obtuse edge perpendicularly truncated by *m*; the ends acuminate by the octahedron *a*, and this truncated by the oblique basic face *p*; *u:u* in front =  $112^\circ$ ; *u:u* (sideways) =  $68^\circ$ ; *u:m* =  $146^\circ$ ; *m:p* =  $113^\circ 45'$  (calc.); *u:p* =  $109^\circ 30'$  (calc.); *a:p* =  $140^\circ$  (obs.); *a:u* =  $149^\circ 30'$  (obs.); *a'':p* =  $115^\circ 48'$  (calculated from the preceding data), =  $115^\circ$  (obs.); *a':u* =  $134^\circ 42'$  (calc.) =  $135^\circ 30'$  (obs.) (Laurent). Melts at about  $190^\circ$  (Laurent); at  $182^\circ$  and solidifies in the crystalline state at  $181^\circ$  (Jacquelin). Grates between the teeth. Inodorous, but has a rather sweet taste (Laurent). No rotatory power (Biot, Jacquelin). Neutral. Sublimes under the same circumstances as mannite (Berthelot). (See *Melampyrite* in the Appendix.)

				Laurent.		Jacquelin.	
				<i>earlier.</i>	<i>later.</i>		
12 C	72	...	39.56	...	38.14	39.20	39.69
14 H	14	...	7.69	...	7.66	7.61	7.70
12 O	96	...	52.75	...	54.20	53.19	52.61
$C^{12}H^{14}O^{12}$ ...				182	...	100.00	100.00

Laurent and Jacquelin formerly gave other formulæ. Soubeiran (*Compt. rend.* 30, 339) regarded dulcite as identical with mannite, and Laurent then recognised its isomerism with mannite.

*Decompositions.* 1. When heated above  $190^\circ$ , it gives off about 9 per cent. of water; if the loss amounts to 10 per cent., the residue becomes coloured and gives off empyreumatic products, but if dissolved in water, yields unaltered crystals of dulcite (Laurent). Under these circumstances, dulciten is doubtless formed, and then reconverted into dulcite, as Berthelot (*Chim. organ.* 2, 209) also supposes. (Is this view supported by experiment?) Dulcite heated to  $275^\circ$  gives off carbonic oxide without much colouring; between  $280^\circ$  and  $290^\circ$ , it evolves large quantities of gas smelling of acetic acid and acetone (Jacquelin). Dulcite yields, by dry distillation, the same products as mannite, but does not leave any carbonaceous residue (Laurent).—2. Heated in small quantities on platinum-foil, it appears to boil, giving off gases and vapours of dulcite, which take fire and burn completely away (Jacquelin).—3. Dry chlorine gas does not act on dulcite in sunshine, even when passed into its solution heated to  $40^\circ$ ; but when chlorine gas is passed over dulcite in the fused state, hydrogen is abstracted and hydrochloric acid is formed, part of this acid remaining united with the undecomposed portion of the dulcite in the form of a conjugated acid (Jacquelin). When the product formed by chlorine is dissolved in water,—whereupon loose brown flocks separate,—the solution filtered, the excess of chlorine expelled by boiling, the hydrochloric acid completely precipitated by an equivalent quantity of sulphate of silver, and the sulphuric acid by baryta-water, there remains a neutral liquid containing baryta and likewise hydrochloric acid, precipitable by sulphuric acid and sulphate of silver. If this liquid be again mixed with sulphate of silver, chloride of silver is formed, together with a soluble silver-salt which, when evaporated in vacuo, remains behind as an

uncrystallisable, sticky mass (Jacquelin).—4. With *biiodide of phosphorus*, dulcite behaves like mannite (Berthelot, *Chim. organ.* 2, 208).—5. *Nitric acid* converts it into mucic acid (Laurent). Dulcite, boiled with nitric acid according to Liebig's method (see *Milk-sugar*, p. 220), yields mucic, oxalic, and racemic acids. As long as the formation of the latter acid goes on, the solution contains a substance which reduces potassio-cupric tartrate in the same manner as grape-sugar. Whilst therefore milk-sugar, treated with nitric acid, yields (dextro-) tartaric acid, dulcite, treated in like manner, yields (inactive) racemic acid. (Carlet, *Compt. rend.* 51, 137, and 53, 343).—6. From the solution in *fuming nitric acid*, dulcite is precipitated by adding *oil of vitriol*, and pouring in water, as hexnitrodulcite (Béchaup, *Compt. rend.* 51, 257). Water does not precipitate the nitric acid solution.

7. Dulcite dissolves slowly and without colouring in *oil of vitriol* and forms dulcisulphuric acid. The solution, if heated above 40° or 50°, blackens and gives off carbonic and sulphurous acids (Jacquelin). According to Berthelot, dulcite is not carbonised at 100°, either by oil of vitriol or by fuming *hydrochloric acid*. Oil of vitriol, diluted with 20 pts. of water, likewise forms a small quantity of dulcisulphuric acid, when heated to 100° for six hours, without altering the rest of the dulcite. When the solution of dulcite in oil of vitriol is diluted with water, and neutralised with carbonate of baryta, a solution of dulcisulphate of baryta is obtained, which, after evaporation in vacuo, remains as a translucent, adhesive mass having a bitter and sharp taste, soluble in dilute alcohol, less soluble in absolute alcohol and insoluble in ether, not precipitable from its solutions by aqueous nitrate of lead or nitrate of silver. From its solution, mixed with basic acetate of lead, alcohol throws down dulcisulphate of lead.

8. Dulcite heated with *acetic*, *butyric*, *benzoic* or *stearic acid* to 200°, or with tartaric acid to 100°, forms peculiar compounds called *Dulcitanides*, which resemble the mannitanides (p. 362) in all respects, and like the latter, take up water and are resolved into dulcitan and acid. (Berthelot, *Compt. rend.* 41, 452.)

9. Dulcite boiled with dilute *potash-ley* (or concentrated, according to Jacquelin) is dissolved, and crystallises unaltered on cooling. (Laurent.) Very strong potash-ley, at the boiling heat, forms, with dulcite a syrup which is not precipitated by alcohol (Laurent). When dulcite, is fused with *hydrate of potash*, or subjected to dry distillation with *potash-lime*, hydrogen is evolved, mixed with small quantities of ammonia (from the cyanogen in the potash, Kr.) and marsh-gas; sometimes also an oil smelling like acetone passes over. In the residue there remain carbonate of potash, a large quantity of oxalate and a small quantity of butyrate, the latter recognisable by its odour after supersaturation with sulphuric acid (Jacquelin).—10. From *potassio-cupric tartrate*, dulcite does not precipitate cuprous oxide, even after boiling with acids (Berthelot).

11. Dulcite does not ferment in contact with yeast. (Soubeiran, Jacquelin.) It undergoes the same decomposition as mannite (p. 365), into alcohol, lactic acid and butyric acid, when left in contact for some weeks at 40° with *cheese* (or pancreas tissue) and *chalk*; like mannite

it also forms a peculiar sugar by contact with testicular tissue (Berthelot, *N. Ann. Chim. Phys.* 50, 348 and 372).

*Combinations.* Dulcite dissolves readily in *water*, and crystallises from the boiling saturated solution on cooling.—Aqueous dulcite dissolves *lime* (Berthelot).

*With Baryta.*—Baryta-water is added to aqueous dulcite, and the solution is concentrated in a flask. On cooling, it deposits four-sided prisms, terminated by an acute pyramid with rectangular base. They must be quickly washed with aqueous alcohol. This compound gives off 27.4 p. c. water at 170° and contains 29.7 p. c. barium, agreeing with the formula  $C^{12}H^{14}O^{12}, 2BaO + 14 aq.$  (calc. 27.33 p. c.  $H_2O$  and 29.71 Ba). (Laurent.)

Dulcite is not precipitated by aqueous *acetate of lead*, either *neutral* or *basic* (Laurent), by *nitrate of silver*, or by *terchloride of gold*, and is not altered by either of these reagents, even at the boiling heat. (Jacquelain.) From its concentrated aqueous solution, it is precipitated by *ammoniacal sugar of lead* (Berthelot).

Nearly insoluble in boiling *alcohol* (Laurent).

#### *Appendix to Dulcite.*

#### **Dulcitan.**



BERTHELOT. *Chim. organ.* Paris, 1860, 2, 209.

#### *Dulcinane.*

Obtained by heating dulcite for some time to near 200°, or by the decomposition of dulcitanides, in the same manner as mannitan (p. 369) from mannite and mannitanides, and purified in the same manner as mannitan.—A viscid syrup, probably dulcitan, is obtained by reducing hexnitro- and quadrinitrodulcite with ferrous salts (Béchamp, *Compt. rend.* 51, 258).

Scarcely fluid, neutral syrup, which volatilises perceptibly at 120°, and is partially converted into dulcite by prolonged contact with *water*, or by heating with *baryta-crystals* and water.

Soluble in *water* and in absolute *alcohol*, but not in *ether*.

#### *Conjugated Compounds of Dulcite.*

#### **Butyro-dulcitan.**



BERTHELOT. *Chim. organ.* 2, 210.

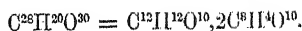
*Dulcite butyrique, Buttersäuredulcitanester.*—Obtained from butyric  
2 c 2

acid and dulcite at  $120^{\circ}$ , in the same manner as acetomannitan (p. 375), from mannite and acetic acid, and purified like that compound.

Colourless, inodorous, viscid oil which tastes bitter and also like butyric acid. Neutral. — Decomposed by *alcoholic hydrochloric acid*, into dulcitan and butyrate of ethyl.

Sparingly soluble in *water*, easily in *alcohol* and *ether*.

### Dulcitartaric Acid.



BERTHELOT. *N. Ann. Chim. Phys.* 54, 77.

Known only as a lime-salt, which is prepared in the same manner as manni-tartrate of lime. This salt, after drying in vacuo, retains water of which 11·7 p. c. goes off at  $110^{\circ}$  (8 at. by calculation = 11·8 p. c.).

	at $110^{\circ}$ .			Berthelot.		
28 C .....	168	...	31·23	.....	31·6	
26 H .....	26	...	4·83	.....	5·3	
36 O .....	288	...	53·53	.....	53·3	
2 CaO .....	56	...	10·41	.....	9·8	
<hr/>						
$C^{28}H^{18}Ca^2O^{30}, 8HO$ .....	538	...	100·00	.....	100·0	

After drying in vacuo, it is therefore  $C^{28}H^{18}Ca^2O^{30} + 16HO$ .

### Benzo-dulcitan.



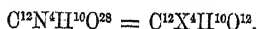
BERTHELOT. *Chim. organ.* 2, 211.

*Dulcite benzoïque, Benzodulcitanester.*—Obtained from dulcite and benzoic acid, like acetomannitan (p. 375), from mannite and acetic acid.

Neutral resin, resembling turpentine; decomposed by *alcoholic hydrochloric acid*, with formation of benzoate of ethyl; by *hydrate of lime* into benzoate of lime and a mixture of dulcite and dulcitan, amounting to 47 per cent.

Insoluble in *water*, easily soluble in *ether*.

### Quadrinitro-dulcite.



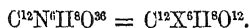
BÉCHAMP. *Compt. rend.* 51, 257; *Zeitschr. Ch. Pharm.* 3, 657.

Hexnitrodulcite is completely converted into this compound without alteration of crystalline form, by the spontaneous decomposition which it undergoes, with evolution of nitrous vapours, when kept for a month between  $30^{\circ}$  and  $45^{\circ}$ .

Needles harder and less flexible than those of hexanitrodulcite; crystallises from alcohol, in beautiful translucent prisms.—Melts to a pasty mass at 130°, completely at 140°, and gives off red fumes at 145°.

It is reduced by *ferrous salts* and forms a non-crystallisable syrup, probably dulcitan.

### Hexnitro-dulcite.



BÉCHAMP. *Compt. rend.* 51, 257.

*Dulcine trinitrique* =  $C^6H^4O^3, 3NO^5$ . (Béchamp.)

A solution of dulcite in 5 pts. fuming nitric acid is mixed with 10 pts. oil of vitriol, and the mixture, which becomes turbid, is immediately thrown into a large quantity of water. The semifluid precipitate solidifies slowly to a buttery mass, which, after washing with water, crystallises from alcohol in needles.

Beautiful, colourless, flexible needles, which melt between 68° and 72°.

Gives off nitric acid vapours continuously and is in the end wholly converted into quadrinitro-dulcite. — When heated to 90°, it is converted, with regular emission of red vapours, into a pasty mass, and then into a hard, friable, white, acid product.

*Saccharoidal Substance*  $C^{12}H^{16}O^{13}$ .

### Melampyrite.\*



HÜNEFELD. *J. pr. Chem.* 7, 233; 9, 47; abstr. *Berz. Jahresber.* 17, 312.

W. EICHLER. *Ueber das Melampyrin*, Moskau, 1855; abstr. *Lieb. Kopp. Jahresber.* 1856, 665; *N. Repert.* 7, 259; *Chem. Centr.* 1859, 522; *Rép. Chim. pure*, 2, 103.

*Melampyrin*. — Found in the herb of *Melampyrum nemorosum* (Hünefeld), also of *Scrophularia nodosa* and *Rhinanthus Crista Galli* (Eichler).

*Preparation*. The decoction of the dried herb taken at the flowering time is mixed with milk of lime till it exhibits an alkaline reaction, then boiled up, filtered, concentrated to a small bulk, and acidulated with hydrochloric acid. On cooling and further crystallisation, melampyrite crystallises out, and may easily be obtained pure by recrystallisation from water (Eichler). — 2. The dried herb is boiled with water

\* A paper by Dr. L. Gilmer, showing that Melampyrite is identical with Dulcite (p. 384) has just appeared (*Ann. Pharm.* Sept., 1862),—too late for insertion in the text. The results will be given in the Appendix to this volume.



containing hydrochloric acid, the decoction is strained, mixed with milk of lime till it exhibits a slight alkaline reaction, then concentrated, —whereupon it deposits succinate of lime,—and the lime-compound of melampyrite, which passes into the filtrate, is decomposed with hydrochloric acid; it then deposits crystals, which may be purified by recrystallisation (Eichler).—Hünefeld evaporates the decoction to a syrup, and leaves the melampyrite to crystallise out; removes from the mother-liquors the substances precipitable by neutral and basic acetate of lead, and the excess of lead by hydrosulphuric acid, and again evaporates. Eichler, instead of proceeding in this manner, precipitates the decoction with neutral acetate of lead, boils the filtrate with lead-oxide, removes dissolved lead by hydrosulphuric acid, and evaporates.

*Properties.* Colourless, transparent prisms, generally united into crusts. Less sweet than milk-sugar. Sp. gr. 1.466 at 15°. Melts at 186°, without loss of weight, to a clear liquid, which, on cooling, solidifies to a crystalline mass, with cauliflower-like excrescences. Neutral. Destitute of rotatory power (Eichler).

<i>at 100° or melted.</i>				Eichler. <i>mean.</i>
12 C .....	72 .....	37.70 .....	37.70 .....	37.79
15 H .....	15 .....	7.85 .....	7.85 .....	7.83
13 O .....	104 .....	54.45 .....	54.45 .....	54.38
$C^{12}H^{16}O^{13}$ .....	191 .....	100.00 .....	100.00 .....	100.00

*Decompositions.* 1. Fused melampyrite becomes slightly brown when heated to 180°, but still solidifies in the crystalline form on cooling, the loss of weight amounting to about 1 per cent.—2. Heated on platinum-foil, it emits a faint odour of caramel, takes fire and burns with a white flame.—3. It dissolves in *oil of vitriol*, forming melampyro-sulphuric acid, the solution turning brown when heated.—4. It dissolves easily in warm *nitric acid* of sp. gr. 1.32 and crystallises on cooling apparently without alteration. On heating the solution, nitrous fumes are given off, and mucic and oxalic acids are formed.—The solution of melampyrite in cold *nitro-sulphuric acid* yields, on addition of water, an oil which dissolves in alcohol and ether, leaving a white powder. The latter is obtained almost alone by the action of only 6 pts. nitrosulphuric acid continued for one day, whereas from 10 to 15 pts. acid acting for 2 or 3 days at 20°–25° forms chiefly the product soluble in ether, which, however, is itself a mixture of a crystallisable and an oily nitro-compound. From the pulverulent nitro-compound insoluble in ether, melampyrite-ammonia is formed by the action of sulphide of ammonium (Eichler).

Melampyrite is not decomposed by boiling with dilute acids or alkalis, or by potassio-cupric tartrate. It is not altered by heating with dilute sulphuric acid and bichromate of potash, and when mixed with potash-ley, does not reduce mercuric oxide. It does not ferment with yeast. (Eichler.)

*Combinations.* Melampyrite dissolves in 25.5 pts. of water at 15°, easily in boiling water.

Melampyrite combines with *bases*. The compounds with the alkalis and alkaline earths are soluble in water, those with lead-oxide and

cupric oxide are insoluble. Aqueous melampyrite does not precipitate metallic salts. (Eichler.)

*With Ammonia.* — Melampyrite crystallises, unaltered, from hot aqueous ammonia, or after being heated with it to  $120^{\circ}$ ; but when nitromelampyrite (p. 390) is decomposed by sulphide of ammonium, or when the baryta- or lime-compound of melampyrite is decomposed by carbonate of ammonia, the concentrated filtrate yields transparent, colourless right prisms, which have an alkaline reaction, do not give off ammonia at  $100^{\circ}$ , but become carbonised at higher temperatures, with loss of ammonia and without previous fusion, and are decomposed by acids into melampyrite and an ammonia-salt. These crystals are easily soluble in water. (Eichler.)

*Potash-compound.* — Warm alcoholic potash dissolves melampyrite, and the solution, when left to itself, deposits needles, which, having a caustic alkaline taste, are easily soluble in water, absorb water and carbonic acid from the air, and are converted into a mixture of melampyrite and carbonate of potash. (Eichler.)

*Soda-compound.* — Small flat needles, resembling the potash-compound, but less soluble in alcohol.

*Baryta-compound.* — When melampyrite is heated with water and baryta-crystals, a clear solution is formed, which, on cooling, deposits six-sided prisms. Easily soluble in warm water, less soluble in alcohol, which, however, does not precipitate the aqueous solution. Gives off 26.73 p. c. water at  $120^{\circ}$ . (Eichler.)

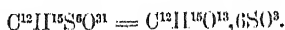
				Eichler.
$C^{12}H^{15}O^{13}$ .....	191.0	....	40.64	
2 BaO .....	153.2	....	32.58	..... 32.05
14 H <sub>2</sub> O .....	126.0	....	26.78	..... 26.73
<hr/>				
$C^{12}H^{16}O^{13}, 2BaO + 14aq$ .....	470.2	....	100.00	

Aqueous melampyrite dissolves *lime*. — Melampyrite does not combine with *magnesia*.

*Lead-compound.* — An aqueous solution of melampyrite is not precipitated by acetate of lead, either neutral or basic. From an ammoniacal solution of the neutral acetate, aqueous melampyrite throws down a white precipitate, which after drying at  $100^{\circ}$  in a stream of hydrogen, contains 77.68 p. c. lead-oxide, corresponding to the formula  $C^{12}H^{16}O^{13}, 6PbO$ , which requires 77.84 p. c. PbO. (Eichler.)

*Copper-compound.* — Melampyrite boiled with cupric sulphate and potash yields a clear blue solution. — From aqueous melampyrite an ammoniacal solution of cupric sulphate throws down a light blue precipitate, which after washing with weak aqueous ammonia, turns green at  $100^{\circ}$ , and contains 55.25 p. c. cupric oxide, agreeing therefore with the formula  $C^{12}H^{16}O^{13}, 6CuO$ , which requires 55.49 p. c. CuO. (Eichler.)

Melampyrite dissolves in 1362 pts. *alcohol* of sp. gr. 0.835. From the solution in boiling alcohol, a few transparent crystals separate on cooling. It is slightly soluble in *acetone*, *wood-spirit*, *chloroform*, and *acetate of ethyl*, insoluble in *ether*, *benzene*, *oil of turpentine*, and *rock-oil*. (Eichler.)

*Conjugated Compounds of Melampyre.***Melampyro-sulphuric Acid.**

EICHLER, *loc. cit.*

The solution of melampyre in oil of vitriol, diluted with water, saturated with carbonate of lead, filtered from sulphate of lead and decomposed by hydrosulphuric acid, then filtered from the sulphide of lead and evaporated, yields melampyro-sulphuric acid in the form of a syrup, which has a faint yellow colour, a sour and bitter taste, and carbonises when heated, evolving sulphurous acid.

*Melampyrosulphate of Baryta.*—Obtained by dissolving melampyre in oil of vitriol, diluting with water, neutralising with carbonate of baryta, and evaporating the filtrate at a very gentle heat.—In the moist state it is a mass having the consistence of turpentine; after drying in vacuo it forms a transparent gum which dissolves readily in water and is precipitated by alcohol. Decomposes at 100°.

	Eichler.			
$C^{12}H^{12}O^{10}$ .....	164.0	...	25.88	
3 BaO .....	229.8	...	36.26	36.45
6 SO <sup>3</sup> .....	240.0	...	37.86	37.79
<hr/>				
$C^{12}H^{12}Ba^3O^{13}, 6SO^3$ .....	633.8	...	100.00	

The lime-salt resembles the baryta-salt, but is not precipitated by alcohol from the aqueous solution. It does not precipitate either *basic acetate of lead*, *mercurous nitrate*, or *nitrate of silver*. (Eichler.)

*Appendix to the Carbo-hydrates.***Pectin.**

VAUQUELIN. *Ann. Chim.* 5, 100; 6, 282. — *Ann. Chim. Phys.* 41, 46.

PAYEN. *J. Pharm.* 10, 390.

BRACONNOT. *Ann. Chim. Phys.* 28, 173; 30, 96; *Schw.* 44, 141; 45, 400; *N. Tr.* 11, 1, 56; 13, 1, 126; *J. Chim. méd.* 1, 509; 15, 166. — *Ann. Chim. Phys.* 47, 266; *N. Tr.* 25, 2, 167. — *Ann. Chim. Phys.* 72, 433.

GUIBOUT. *J. Chim. méd.* 1, 27; *Schw.* 44, 136; *abstr. Mag. Pharm.* 11, 41.

MULDER. *Pogg.* 44, 432; *J. pr. Chem.* 14, 277. — *J. pr. Chem.* 16, 246.

FREMY. *J. Pharm.* 26, 368; *Ann. Pharm.* 35, 312; *J. pr. Chem.* 21, 1. — *N. Ann. Chim. Phys.* 24, 9; *Ann. Pharm.* 67, 257; *J. pr. Chem.* 45, 389; Preliminary notice, *Compt. rend.* 24, 1046; *N. J. Pharm.* 12, 13.

SOUBEIRAN. *N. J. Pharm.* 11, 417; *J. pr. Chem.* 41, 309; *Pharm. Centr.* 184, 513.

POUMARÈDE & FIGUIER. *Compt. rend.* 23, 918; *N. J. Pharm.* 11, 458. — *Compt. rend.* 25, 17; *N. J. Pharm.* 12, 81; *Ann. Pharm.* 64, 387; *J. pr. Chem.* 42, 25.

CHODNEW. *Ann. Pharm.* 51, 356.

FR. JOHN. *N. Br. Arch.* 45, 24, and 129.

*Vegetable jelly, Gelée végétale, Grossuline, Pflanzengallerte.*

Vauquelin showed, in 1790, that the expressed juice of tamarinds and other fruits solidifies, when left at rest, to a transparent jelly, which may be purified by draining off the juice and washing. This jelly, which was then likewise separated by Vauquelin, Bostock, and John from other fruits, is sparingly soluble in cold water, easily in hot water, and in alkalis, and may, therefore, be regarded as pectosic acid. Braconnot, in 1824, by exhausting plants with alkalis and precipitating the extract with acids, obtained pectic acid (or pectosic acid); respecting which he showed, in 1832, that it does not constantly occur ready formed, and not in all fruits, being more frequently produced by the action of alkalis on pectin. Since that time the most exact experiments on pectous substances have been made by Fremy. — The statements of Chodnew and of Poumarède & Figuier cannot with certainty be applied to either of Fremy's pectous substances in particular. Chodnew's pectin is most nearly related to Fremy's parapectin; his pectous and hyperpectic acids do not agree exactly with either of Fremy's pectous substances. — According to Mulder, pectin and pectic acid are distinguished from one another by the different quantities of inorganic matter which are united in them with the organic substance. The former may be regarded as a neutral, the latter as an acid salt.

*Occurrence and Formation.* Many fruits in the unripe state, fleshy roots and other parts of plants (*vid. inf.*) contain a substance insoluble in water, alcohol, and ether: Fremy's *pectose*, which, during the ripening of the fruit or by boiling with water, acids, or alkalis, yields the several pectous substances. Of the latter, pectin, parapectin (and perhaps pectic acid) are found in the ripe fruit, while the over-ripe fruit contains salts of metapectic acid.

Pectous substances occur in lemons, oranges, currants, gooseberries, bilberries, and the fruit of *Solanum lycopersicon* (Vauquelin, Bostock, John); in apples, pears, plums, and apricots, in the cucumber and the fruits of other cucurbitaceous plants (Braconnot), in the tubers of *Dahlia pinnata*, *Helianthus tuberosus*, and the bulbs of *Allium Cepa*; in the roots of *Scorzonera hispanica*, *Apium graveolens*, *Daucus Carota*, *Brassica Napus*, *Paeonia officinalis*, *Thlonis tuberosa*, *Rumex Patientia*, *Spiraea filipendula* (Braconnot), *Gentiana lutea* (Denis, *J. Pharm.* 22, 304); in the root-bark of *Aylenthus glandulosa* (Payen), in the stalks and leaves of herbaceous plants, in maple-wood, in the inner bark of all trees, in the seeds, and, generally in every plant (Braconnot). The fruit of *Arbutus Unclo* contains parapectin (Fihol, *Compt. rend.* 50, 1185). Cinchona-barks contain pectin, according to Veltmann (*Schw.* 54, 388), and Reichel (*Ueber Chinurinden u. deren chem. Bestandth.* Leipzig, 1856); according to Reichhardt (*N. Br. Arch.* 92, 12), they do not.

*Calluna vulgaris* and *Erica herbacea* contain a pectous substance; *Lectum palustre* contains a mixture of pectin and parapectin (Rochleder, *Wien. Akad. Ber.* 9, 312). (On jellies from pine needles, pine-bark, and *Thuja occidentalis* see vol. xiii, pp. 239, 240, the jellies from yellow pods and the fruit of *Syringa* are described in this Appendix). — A jelly from *Fucus crispus* was examined by Mulder (*J. pr. Chem.* 15, 293) and Herberger (*Repert.* 49, 348); another from *Fucus amygdaceus* by Riegel (*Jahrb. pr. Pharm.* 6, 8), from *Rivularia tubulosa* by Braconnot (*Ann. Chim. Phys.* 70, 206).

The existence of pectose in plants is demonstrated by the following observations:—

Pectin is precipitated by alcohol from the juice of ripe, but not of unripe fruits. When the pulp of unripe fruits is washed with water

as long as the water runs off acid, and the residual mass is boiled with water, no pectin passes into the solution, but boiled unripe fruits, or the solutions obtained by boiling unwashed fruit-pulp with dilute acids, or acid fruit-juice, are rich in pectin (Fremy).

When fruit-pulp or roots are macerated for several days with strong hydrochloric acid, the solution contains only traces of pectin, but if they are boiled for some minutes with slightly acid water, the pectin passes into solution. In this case, insoluble compounds of pectin, if such had existed in the fruit-pulp, must have been decomposed without the aid of heat (Fremy).

During the ripening of fruits, the cellular tissue, which is at first thick and formed of several superposed membranes, becomes thinner, and is converted into soluble products, at the same time that the incrusting layers of pectose dissolve in the form of pectin. If a thin slice of the fruit be placed under the microscope in contact with aqueous cuprammonia for some hours, the woody fibre dissolves, the insoluble residue still exhibits the form of the cells, and is formed of green cupric pectate, which is decolorised by acids, with separation of pectic acid. In this case, the pectic acid is formed from pectose, whereas the same substance, when treated with dilute acids, dissolves as pectin, and when boiled with milk of lime, as metapectic acid (Fremy).

The observations of Soubeiran and Chodnew (*vid. inf.*) do not quite agree with those of Fremy. When peeled quinces, not perfectly ripe, are rubbed to a pulp, the juice filtered off, boiled up, filtered again, cooled, and mixed with a large quantity of alcohol, only a very small quantity of jelly is produced. If the remaining substance be washed, and, while still acid, boiled for some minutes with water, and finally again with hydrochloric acid, a jelly is again obtained. Perfectly ripe quinces yield but a small quantity of jelly when their juice is precipitated with alcohol, but a large quantity when the entire fruit is boiled with water. The jelly, after being washed with alcohol, dissolves but partially in water, a portion not dissolving till it has again been boiled with acidulated water. From the juice of other fruits, also, alcohol precipitates pectous substances only partly soluble in water (Soubeiran). See also other experiments of the same kind by Soubeiran (*N. J. Pharm.* 11, 418 and 12, 420).

Chodnew obtains from washed roots or unripe fruits, by boiling with hydrochloric acid, not pectin, but the substance which he calls *pectous acid* (p. 396), afterwards from the substances thus exhausted with acids, hyperpectic acid may be extracted by boiling with potash-ley (not with ammonia). He regards both these bodies, pectous acid  $C^{28}H^{21}O^{25}$ , and hyperpectic acid  $C^{28}H^{19}O^{27}$ , as existing ready-formed in the fleshy part of the fruit and in the root, and as capable of yielding pectic acid, when these substances are boiled without having been previously exhausted with acid, according to the equation  $C^{28}H^{21}O^{25} + C^{28}H^{19}O^{27} = 2C^{28}H^{20}O^{26}$ . But, since his pectous acid is converted into pectic acid by solution in potash-ley and precipitation with acids, a change which appears to take place without evolution of hydrogen or absorption of oxygen, the two acids cannot stand to one another in the relation indicated by the formulæ above given. Pectous acid, according to Chodnew, occurs in turnips in combination with lime, and may be extracted by boiling water after the lime has been removed by cold hydrochloric acid.

*Preparation.* The expressed and filtered juice of very ripe pears is treated with oxalic acid to precipitate the dissolved lime, and with tannic acid to precipitate albumin, and the filtrate is mixed with alcohol which precipitates pectin in long threads. These are purified by washing with alcohol, repeated solution in cold water, and precipitation with alcohol, till neither sugar nor an organic acid can be detected in the solution (Fremy). Pure pectin leaves no residue when it is treated with excess of baryta-water, and the solution filtered from the pectate of baryta is evaporated (Fremy.)

Braconnot boils the recently expressed juice of ripe apples for a while to coagulate the albumin, precipitates the filtrate with alcohol, and purifies it by repeated solution in water and precipitation with alcohol.

Guibourt leaves currant-juice to ferment slightly and solidify to a jelly, and boils the jelly with alcohol. The product thus obtained is probably pectosic acid (Kr.).

Poumarède & Figuier leave comminuted gentian roots to soften in warm water, wash them thoroughly with water and very dilute acetic acid, and digest the roots thus prepared with very dilute acetic acid at  $80^{\circ}$ — $90^{\circ}$  for half or three-quarters of an hour, and precipitate the solution with alcohol of  $36^{\circ}$ . The precipitated pectin, purified by pressure, repeated solution, and precipitation and washing with alcohol and ether, is a neutral, light, fibrous substance yielding from 8 to 9 p. c. ash and containing at  $120^{\circ}$ , on the average, 43.38 p. c. carbon, 5.67 hydrogen, and 50.95 oxygen; according to Poumarède & Figuier, it is isomeric with cellulose. It is not blackened by oil of vitriol, it is converted into pyroxylin by nitrosulphuric acid, and it reduces ferric salts. From its aqueous solution it is precipitated by concentrated aqueous alkalis and by many salts. After its aqueous solution has been treated with very dilute potash, it is not precipitated by acids as pectic acid, but may be recovered with all its properties by addition of alcohol. The transformation of pectin into pectic acid does not take place till the mineral substances contained in the former have undergone a transformation [of what kind? Kr.].—From carrots Poumarède & Figuier obtain a pectin [different from the former?] by washing the root-pulp with water and dilute acetic acid, then boiling it with dilute carbonate of soda, neutralising with hydrochloric acid, and precipitating with alcohol. This pectin likewise dissolves in water, and contains, at  $120^{\circ}$ , 43.33 p. c. carbon, 5.66 hydrogen, and 51.01 oxygen.

Mulder precipitates the expressed and filtered juice of apples with alcohol and boils the precipitate with alcohol to remove sugar, malic acid and tannin. Such pectin from sweet apples, after deduction of 5.9 p. c. ash, contains 44.59 p. c. carbon, 5.35 hydrogen and 50.06 oxygen; from sour apples, after deduction of 9.3 p. c. ash, 45.23 C., 5.47 H., and 49.30 O. It is precipitated on agitating its aqueous solution with hydrated lead-oxide, also by basic acetate of lead. The latter precipitate contains 56.62 p. c. lead-oxide, and after deduction of this, 45.00 p. c. C., 5.37 H., and 42.53 O. (What becomes of the ash? Kr.).

Chodnew obtains *pectin*: a. By boiling crushed pears with water, precipitating the filtered juice with alcohol, and washing with alcohol and ether, whereby it becomes opaque, and acquires the texture of woody fibre, yields after drying at  $115^{\circ}$ , 8.63 p. c. ash, and after deduction of this, 46.04 p. c. C., 5.50 H., and 48.46 O. This pectin is not precipitated by chloride of barium, but it is precipitated by neutral acetate of lead and sulphate of copper, and therefore agrees with

Fremy's parapectin (p. 399). — *b*. Or he obtains it by boiling the expressed juice of bruised apples, precipitating with alcohol, redissolving in water, mixing the solution with hydrochloric acid, and precipitating with alcohol. It contains 1.6 p. c. ash, and after deduction of this, 43.75 p. c. C., 5.52 H., and 50.73 O. This pectin resembles that obtained by *a*, but has a slight acid reaction and sometimes reduces an alkaline solution of cupric oxide. Its lead-compounds contain 23 and 33.45 p. c. PbO. Pectin prepared from pears, according to *b*, contains 1.23 p. c. ash and 43.79 p. c. C., 5.84 H. and 50.37 O. Chodnew gives the formula  $C^{28}H^{21}O^{24}$ .

Chodnew's *pectous acid* is obtained from the washed pulp of turnips or apples, by boiling with hydrochloric acid and precipitating with alcohol, after which it is washed with alcohol and ether, pressed and dried at 120°. Non-friable mass, resembling woody fibre, slightly acid, and soluble in water even after drying. Contains 0.83 p. c. ash, and on the average 43.16 p. c. C., 5.60 H. and 51.24 O.; according to Chodnew =  $C^{28}H^{21}O^{24}$ . It is converted into pectic acid by solution in potash-ley and precipitation with hydrochloric acid, precipitated from the aqueous solution as a jelly by excess of potash-ley or lime-water, but not by chloride of potassium. If the solution has been previously mixed with ammonia, chloride of potassium throws down a jelly soluble in hydrochloric acid. From aqueous pectous acid, neutral acetate of lead precipitates a jelly soluble in acetic acid, and when dried at 120°, containing 34.02 p. c. C., 4.22 H., 39.63 O. and 22.13 PbO. ( $C^{28}H^{20}O^{24}$ , PbO, according to Chodnew). A mixture of aqueous pectous acid and nitrate of silver becomes viscid after a while, acquires a faint dark red colour, becoming dark brown-red after addition of a little ammonia and heating; alcohol throws down from the same solution a jelly, which becomes reddish at 100°, and contains 33.62 p. c. C., 4.12 H., 39.05 O. and 23.21 AgO. ( $C^{28}H^{20}O^{24}$ , AgO, according to Chodnew). Chodnew thinks it probable that this pectous acid is identical with pectin. On Chodnew's Hyperpectic acid, see *Pectic acid*.

*Properties.* White amorphous mass, obtained by evaporation of its aqueous solution, in transparent laminae (Braconnot), and by precipitation of its concentrated solution, in threads, from its dilute solution, in the form of a jelly. Neutral. Tasteless. Destitute of rotatory power. (Fremy.)

Calculation according to Fremy.				Fremy. mean.
64 C .....	384	.....	40.67	..... 39.92
48 H .....	48	.....	5.08	..... 5.50
64 O .....	512	.....	54.25	..... 54.58
<hr/> $C^{64}H^{48}O^{64}$ .....				<hr/> 944 .....
				100.00 .....
				100.00

After deduction of about 1 p. c. ash. — Numbers different from those in Fremy's analyses were obtained by Mulder, Chodnew, and Poumarède & Figuier, who have also proposed other formulæ (see above). Gerhardt (*Compt. chim.* 1849, 62) gave the formula  $C^{32}H^{24}O^{30}, 2HO$ ; Berzelius (*Jahresber.* 24, 373) gave  $C^{24}H^{16}O^{20}$ ; Gmelin  $C^{24}H^{18}O^{24}$ . If these formulæ were adopted, those of all the other pectous substances would require alteration. Fremy's formulæ for the whole of the pectous substances are also considered doubtful by many chemists.

*Decompositions.* When pectin (or one of the other pectous substances) is heated to 200°, carbonic acid and water are evolved, and

black pyropectic acid is formed. This acid contains 51.32 p. c. C., 5.33 H., and 43.35 O., corresponding to the formula  $C^{14}H^9O^9$  (calc. 50.96 C., 5.46 H. and 43.58 O.); it is insoluble in water, but dissolves with brown colour in aqueous alkalis (Fremy). — Pectin when *burnt*, smells like burning tartaric acid (Fremy). — Pectin boiled with *nitric acid*, is very easily converted into saccharic acid, and by longer boiling, into mucic acid (Fremy). It does not become coloured with nitric acid, yielding mucic acid, but no sugar. (Chodnew). The solution of pectin in strong nitric acid deposits pectic acid on addition of water (Braconnot, *Ann. Chim. Phys.* 52, 294).

Under the influence of *water, acids or alkalis*, pectin suffers transformations, taking up or giving off water, or merely suffering molecular alteration, and producing other pectous bodies, those which are first produced frequently undergoing further alteration by the action of the reagent employed. Several of these pectous substances may be obtained directly from pectose.

The substance called *pectase*, which occurs together with pectose in fruits and roots, acts on pectin as a ferment, somewhat in the same manner as emulsin and diastase act on other bodies. It is precipitated by alcohol from the juice of carrots and turnips, and thereby loses its solubility in water. Unripe apples and other fruits contain it in the insoluble state. It is rendered inactive by putrefaction or by prolonged boiling with water (Fremy).

*General view of the transformations of Pectin and the mutual relations of Pectous substances.*

1. *Pectose* heated with dilute acids is converted into pectin, which by longer boiling is transformed into metapeptic acid.

2. By boiling with milk of lime, it is converted into metapeptic acid. Probably pectic acid is formed in the first instance.

3. *Pectin*, when its aqueous solution is left to itself, changes into metapeptic acid. If pectose is likewise present, the change takes place more quickly, pectosic, pectic and metapeptic acid being successively produced.—When pectin is boiled with water, parapectin is produced.

4. Pectin boiled with strong acids, is converted into metapeptic acid.

5. By cold dilute aqueous alkalis, it is converted into pectosic acid, which quickly undergoes further transformation into pectic acid, or by boiling with strong alkalis into metapeptic acid.

6. *Parapectin* boiled with dilute acids is converted into metapeptin; aqueous alkalis convert it into a pectate.

7. *Metapeptin* is converted by alkalis into salts of pectic acid.

8. *Pectosic acid* is converted into pectic acid by boiling with water, either pure or alkaline, or by contact with pectase. — When boiled with aqueous alkalis, it forms metapeptic acid.

9. *Pectic acid* is converted, by long contact with water in the cold,



more quickly at the boiling heat, into parapectic acid, then further into metapeptic acid. Boiling with acids or alkalis likewise converts it into metapeptic acid.

10. *Parapectic acid* in contact with water, is quickly converted into metapeptic acid.

11. *Metapeptic acid* cannot be converted into any other substance of the pectin group.

*Note to 3.* A recently prepared aqueous solution of pectin is not precipitated by neutral acetate of lead, but becomes precipitable thereby after standing for several days. The precipitate at first produced contains 15.67 p. c. lead-oxide; if the same pectin be boiled or left for some time in contact with water, precipitates are formed containing 16.54 and 24.6 p. c., and finally, after very long boiling, 49.42 p. c. lead-oxide.

When aqueous pectin at 30° is mixed with pectase, the solution becomes gelatinous after a while, from separation of pectosic acid. This transformation is likewise produced by insoluble pectase (*vid. sup.*), and takes place even in close vessels and without evolution of gas. The juice of carrots and mangold-wurzel brings about the same decomposition of pectin-solution, probably because it contains soluble pectase; on the other hand, the juice of unripe apples and other unripe fruits does not act upon pectin, whereas the fleshy part of fruits containing insoluble pectase does exert an action upon it. By further alteration the pectosic acid is finally converted into metapeptic acid, unmixed with any other product.

The jelly into which the juice of dried fruits solidifies, dissolves for the most part in boiling water, and then consists of pectin and pectosic acid, formed by the successive transformation of the pectose (under the influence of acids and pectase). If however the fruits are rapidly heated, the pectase may become inactive before it has effected the transformation of the pectin. Other jellies are formed by the solution of peptic acid in the salts of organic acids.

*Note to 4.* No sugar is formed by boiling pectin with dilute acids, even for several hours (Fremy).—Pectin, boiled with a small quantity of hydrochloric or dilute sulphuric acid, becomes rose-red, and on adding alcohol to the solution, nothing is separated but a few flocks which settle down on standing. The solution contains sugar and a soluble baryta-salt, perhaps of malic acid. (Chodnew.)

*Note to 5.* Even the smallest quantity of fixed alkali converts pectin into peptic acid, and larger quantities separate a basic pectate. (Braconnot.) Cold aqueous ammonia, potash, or soda, or a cold solution of an alkaline carbonate, first produces pectosic acid. (Fremy.) Pectin boiled with the carbonates of the alkaline earths, decomposes them and forms soluble compounds, from which the pectin may be recovered. With excess of lime-water, it forms insoluble pectate of lime, no organic substance passing into the solution. By excess of alkali it is instantly converted into peptic acid, which may be precipitated by acids, but when thus obtained is very easily transformed into metapeptic acid. (Fremy.) If a cold aqueous solution of pectin (or pectous acid) be mixed with a small quantity of potash-ley, acids

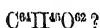
precipitate from it a jelly, which, after washing with dilute hydrochloric acid and alcohol, and drying at  $120^{\circ}$ , dissolves readily in water, and is not precipitated by acids, and therefore does not consist of pectic acid. This jelly yields a lead-salt containing 23.2 p. c. lead-oxide. (Chodnew.) — A boiling aqueous solution of pectin mixed with excess of potash-ley, frequently gives no precipitate with acids, because the pectic acid formed in the first instance has been already converted into metapectic acid.

*Combinations.* Pectin dissolves readily in water. The solution is gummy and very viscid, but if free from albuminous substances, does not solidify to a jelly. (Fremy.)

Pectin unites with the alkaline earths (p. 398). — It is precipitated from its aqueous solution by *basic acetate of lead*, but not by the neutral acetate. (Fremy.) The lead-compound formerly described by Fremy appears to have contained parapectin.

*Alcohol* added to a concentrated aqueous solution of pectin, throws down threads; from a dilute solution it separates a transparent jelly. (Fremy.) Pectin is not precipitated by tincture of galls. (Braconnot.)

### Parapectin.



FREMY. *N. Ann. Chim. Phys.* 24, 14.

Soluble in water, like pectin and metapectin; distinguished from the former by being precipitable by neutral acetate of lead, and from the latter by not being precipitated by chloride of barium (pp. 399 and 400).

Aqueous pectin, when boiled for several hours, loses its gummy consistence, and is converted into parapectin, which is precipitated by alcohol in the form of a translucent jelly. It then still retains albuminous substances, which are precipitated from the aqueous solution by addition of a small quantity of basic acetate of lead.

Amorphous, neutral substance resembling pectin. Tasteless. Isomeric with pectin at  $100^{\circ}$ , but gives up 2 at. water when heated to  $140^{\circ}$ .

	at $140^{\circ}$ .		Fremy.			
			a.	b.	c.	
64 C .....	384	41.48	41.51	42.88	43.77	
46 H .....	46	4.97	5.48	5.68	5.41	
62 O .....	496	53.55	53.01	51.44	50.82	
$\text{C}^{64}\text{H}^{46}\text{O}^{62}$ .....	926	100.00	100.00	100.00	100.00	

a is parapectin several times purified; b and c are less pure.

Parapectin is converted, by boiling with dilute acids, into metapectin; by aqueous alkalis into a salt of pectic acid.

*Lead-compound.* — Aqueous parapectin precipitates neutral acetate

of lead. The precipitate obtained on one occasion contained 11·9 p. c. PbO ( $C^{64}H^{46}O^{62}, HO, PbO = 10\cdot7$  p. c.), in other cases, from 18·8 to 19·6 p. c. or more.

<i>Bibasic.</i>				Fremy.
64 C .....	384·0 .....	33·41 .....	33·06	
46 H .....	46·0 .....	4·00 .....	4·29	
62 O .....	496·0 .....	43·16 .....	43·45	
2 PbO .....	223·4 .....	19·43 .....	19·20	
<hr/>				
$C^{64}H^{46}O^{62}, 2PbO$ .....	1149·4 .....	100·00 .....	100·00	

### Metapectin.



FREMY. *N. Ann. Chim. Phys.* 24, 17.

Soluble in water, like pectin and parapectin; distinguished from both by its acid properties and precipitability by chloride of barium (p. 400).

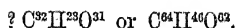
Parapectin is quickly converted into metapectin by boiling with dilute acids. — Uncrystallisable. Has an acid reaction. Metapectin dried at 100°, gives off 2 at. water at 140°.

<i>at 140°.</i>				Fremy.
64 C .....	384 .....	41·48 .....	41·85	
46 H .....	46 .....	4·97 .....	5·58	
62 O .....	496 .....	53·55 .....	52·57	
<hr/>				
$C^{64}H^{46}O^{62}$ .....	926 .....	100·00 .....	100·00	

By *alkalis*, it is converted into a salt of pectic acid. — It dissolves in *water*; if the solution also contains hydrochloric, sulphuric, or oxalic acid, alcohol throws down gelatinous compounds of these acids with metapectin. From aqueous metapectin, *chloride of barium* throws down a precipitate containing from 14 to 15 p. c. BaO ( $C^{64}H^{46}O^{62}, 2BaO = 14\cdot1$  p. c. BaO).

<i>Lead-compound.</i>				Fremy.
64 C .....	384·0 ...	33·41 .....	33·29	
46 H .....	46·0 ...	4·00 .....	4·43	
62 O .....	496·0 ...	43·16 .....	41·98	
2 PbO .....	223·4 ...	19·43 .....	20·30	
<hr/>				
$C^{64}H^{46}O^{62}, 2PbO$ .....	1149·4 ...	100·00 .....	100·00	

### Pectosic Acid.



FREMY. *N. Ann. Chim. Phys.* 24, 22.

Insoluble in cold water, like pectic acid, but distinguished therefrom by its solubility in boiling water (p. 397).

Obtained as the first product of the action of pectase or of aqueous alkalis, on aqueous pectin, the solutions solidifying to a jelly immediately or after addition of acids; but it is quickly converted into pectic acid by the further action of the same agents, or by boiling with water. It has an acid reaction.

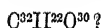
				Fremy.
32 C	192	41.48	41.08	
23 H	23	4.97	5.25	
31 O	248	53.55	53.67	
$C^{32}H^{23}O^{31}$				
	463	100.00	100.00	

It is nearly insoluble in cold water, quite insoluble in water containing hydrochloric acid, but easily soluble in boiling water, and forms a jelly on cooling. The gelatinous amorphous *pectosates* are easily converted into pectates by excess of base; when pure, they dissolve completely in warm dilute acid, whereas pectates leave a residue of pectic acid.

*Pectosate of Baryta*.—Precipitated from aqueous pectin by a quantity of baryta-water insufficient for complete precipitation. Contains, on the average, 24.4 p. c. baryta ( $C^{32}H^{21}O^{29}, 2BaO = 25.3$  p. c.  $BaO$ ).

<i>Pectosate of Lead.</i>				Fremy.
32 C	192.0	28.72	28.82	
21 H	21.0	3.14	3.49	
29 O	232.0	34.72	31.94	
2 PbO	223.4	33.42	32.75	
$C^{32}H^{21}O^{29}, 2PbO$				
	668.4	100.00	100.00	

## Pectic Acid.



BRACONNOT. (1824). *Ann. Chim. Phys.* 28, 173; 30, 96; also *Schw.* 44, 141; 45, 400; *N. Tr.* 11, 1, 56; 13, 1, 126; *Ann. Pharm.* 5 275.—*Ann. Chim. Phys.* 47, 266; *N. Tr.* 25, 2, 167.

REGNAULT. *J. Pharm.* 24, 201; *J. pr. Chem.* 14, 270.

MULDER. *Pogg.* 44, 432; *J. pr. Chem.* 14, 277; 16, 246.

FREMY. *J. Pharm.* 26, 368; *J. pr. Chem.* 21, 1; *Ann. Pharm.* 67, 276.

FROMBERG. *Scheik. Onderzoek.* 2, 31; *J. pr. Chem.* 32, 179; *Ann. Pharm.* 48, 56.

CHODNEW. *Ann. Pharm.* 51. 360.

*Pectinsäure, pectische Säure, Gallertsäure*. Discovered by Braconnot, first analysed by Regnault.

*Occurrence*. Although pectic acid may be obtained from most plants, if not from all, it does not exist in them ready-formed, at least not always (Braconnot), but is produced from pectose or pectin (Fremy). Chodnew is also of opinion that pectic acid does not exist ready-formed in plants, although he explains its formation in a different way (See p. 394).

When carrots, beet, or Swedish turnips are boiled with weak acid,—in order to convert the whole of the pectose into pectin,—so long as pectin remains in solution, alkalis extract little or no pectic acid from the residue; old roots, however, yield a larger quantity than fresh roots. The greater portion of the pectic acid is therefore formed during the reaction; but as pectic acid when boiled with acids is first altered and afterwards dissolved, the experiment is not decisive (Fremy). In another place, Fremy states that fruits and roots yield pectic acid to alkalis, even after exhaustion with acids.

*Formation.* (See page 394.)—On the formation of pectic or parapectic acid according to Schoonbrodt, see *Sugar* (p. 252); on Sacc's pectic acid from wood, see page 413.

*Preparation.* 1. Well washed carrot-pulp is boiled with water slightly acidulated with hydrochloric acid, whereby pectin is dissolved. This pectin is converted into pectate of soda by boiling with the proper quantity of carbonate of soda (to be determined by trial); the solution is precipitated with hydrochloric acid; and the separated pectic acid is dried, first in *vacuo*, then by heat. If too small a quantity of carbonate is added, pectosic acid may be formed; if too much, metapectic acid may be formed (Fremy).—2. The pulp of peeled turnips is well washed with water and pressed, and the residue is boiled for three quarters of an hour with water to which  $\frac{1}{10}$  of carbonate of soda, or a small quantity of hydrate of potash, has been added. The liquid is filtered, the solution is precipitated with chloride of calcium; and the pectate of lime is decomposed by hydrochloric acid (Braconnot, Regnault; Simonin, *J. Pharm.* 20, 478; *Ann. Pharm.* 13, 641). Regnault dissolves the still coloured pectic acid in aqueous ammonia; decolorises it with animal charcoal at 60° to 80°; precipitates the filtrate with hydrochloric acid; and repeats the solution in ammonia and precipitation with acid, in order to remove the mineral constituents.—3. The pulp of carrots or celery is exhausted by washing with pure water, boiling with water containing hydrochloric acid, and again washing with pure water; the residue is boiled with very dilute potash-ley, and the solution is precipitated with hydrochloric acid. (Braconnot). Fremy obtained by this process only a small quantity of pectic acid (*vid. sup.*). Chodnew boils turnips after trituration, washing and pressing, with very dilute potash, for half to three-quarters of an hour; strains; precipitates the still turbid solution with hydrochloric acid; washes the pectic acid several times, first with acidulated, then with pure water; presses it with the hand after each washing, and redissolves it in ammonia, whereby an easily filtering liquid is obtained, which, after filtration, is precipitated with hydrochloric acid. This precipitate is washed as above, and finally with alcohol.

Pectic acid prepared in the ordinary way (probably according to methods 2 and 3) contains albuminous substances which may be more easily precipitated by small quantities of basic acetate of lead, after prolonged boiling of the solution supersaturated with ammonia (Fremy).

Mulder washes comminuted carrots, turnips or sweet apples with water, boils the residue with very dilute potash, not in excess, and precipitates with hydrochloric acid. After purifying the pectic acid by boiling with alcohol, he finds that it has, both in the free state and in combination with acids, the same composition as pectin, containing

after deduction of 3 to 6 p. c. ash, from 44.5 to 45 p. c. carbon, and 5.25 to 5.36 hydrogen. The baryta-salt from sweet apples contains 20.07 p. c., that from turnips 24.01 p. c. BaO; the lime-salt from carrots contains 9.72 p. c. CaO; the lead-salt from carrots, 41.57 p. c. PbO; the cupric salt from carrots contains 18.47 per cent., that from apples 26.28 p. c., that from turnips 17.07 p. c. CuO. This pectic acid immersed in dry ammonia gas takes up 3.43 p. c. ammonia, which escapes at 100°. From these results Mulder regards pectic acid as  $C^{12}H^{18}O^{10}$ , and as identical with pectin (see page 393).

Fromberg prepares his pectic acid from turnips, which he comminutes, washes with cold water, and boils with very dilute carbonate of soda. After precipitation with hydrochloric acid, washing, and drying at 100°, it contains 7 p. c. ash containing carbonic acid; his analyses he calculates, agreeing with Mulder, at 44.58 p. c. carbon, 5.17 hydrogen, and 50.25 oxygen. His lead-salt contains 49.81 p. c. PbO; his copper-salt 16.01 p. c. CuO. On the decompositions with alkalis, page 404. Both Mulder and Fromberg have overlooked the influence which the large amount of ash must have on the proportion of metal in the salts (Kr.).

Chodnew's *Hyperpectic acid* is obtained from turnip-pulp exhausted with hydrochloric acid (see *Pectous acid*, p. 396), by boiling with dilute potash-ley (not with ammonia), and is precipitated as a jelly by hydrochloric acid. It contains at 100°; after deduction of 0.52 p. c. ash, 41.46 p. c. carbon, 4.83 hydrogen, and 53.71 oxygen, and is distinguished from pectic acid by dissolving in aqueous fixed alkalis, but not in ammonia.

*Properties.* Pectic acid in the moist state, is a transparent, colourless jelly, which dries up to a white amorphous mass. Transparent, horny mass, difficult to pulverise (Regnault). Resembles woody fibre and is very friable (Chodnew). Has an acid taste and reaction (Bracconnot, Fremy).

Calculation according to Fremy.				Regnault. at 140°.	Chodnew. at 120°.	Fremy. at 120°.
32 C .....	192	....	42.29	..... 42.69	..... 42.22	..... 41.40
22 H .....	22	....	4.84	..... 4.71	..... 5.24	..... 4.77
30 O .....	240	....	52.87	..... 52.60	..... 52.54	..... 53.83
$C^{32}H^{22}O^{30}$ .....	454	....	100.00	..... 100.00	..... 100.00	..... 100.00

All the analyses are given as mean results. Regnault & Chodnew examined pectic acid prepared from turnips; Fremy analysed acid from various sources. Chodnew's acid left  $\frac{1}{2}$  p. c. ash, which is deducted. — Respecting Mulder's and Fromberg's analyses, see above. Regnault gave the formula  $C^{11}H_7O^{10}$ , both for pectic acid dried at 140° and for that contained in the salts. Chodnew gives the formula  $C^{28}H^{20}O^{26}$ , which agrees with the composition of many of the pectates, and requires 42.42 p. c. carbon, 5.06 hydrogen, and 52.52 oxygen.

*Decompositions* (see p. 397). 1. Pectic acid becomes coloured at 120° (Regnault); black at 150° (Chodnew), and at 200° gives off carbonic acid and water, and is converted into parapectic acid, p. 410 (Fremy). — 2. Melts when heated, swells up, *burns away* and leaves a difficultly combustible charcoal. (Regnault.) Burns without swelling up. (Chodnew.) — 3. When pectic acid is boiled with *water*, parapectic acid is formed, likewise when insoluble pectates are boiled with water. (Fremy.) When

pectic acid is left in contact with water for two or three months, it dissolves as metapectic acid, which is likewise produced when pectic acid is boiled with water for 36 hours, or when moist pectic acid is dried by heat. Not a trace of sugar is formed, even after boiling with water for 7 or 8 days, and the solution does not reduce potassio-cupric tartrate unless it contains para- or metapectic acid. (Fremy.) See below. When moist pectic acid is washed on a filter with boiling water, the filtrate yields with neutral acetate of lead, a precipitate containing 30.5 p. c.  $PbO$ ; after boiling the residue left in the filter for two hours, a lead-salt is obtained, containing 35.5 p. c.  $PbO$ ; and after one hour's boiling, a precipitate with 41.9 p. c.  $PbO$ . The organic substance of all these lead-salts exhibits the composition of pectic acid (or of the isomeric para- or metapectic acid). (Fremy.)

4. Pectic acid is not altered by cold *oil of vitriol*, but is quickly charred by that liquid when heated. (Braconnot, Regnault.)—By boiling with *dilute acids*, it is converted into metapectic acid, which dissolves. (Fremy.)

It is not altered by hot very dilute *hydrochloric acid*. (Regnault.)—Pectic acid prepared from turnips does not dissolve till after very long boiling with dilute acids (more quickly with concentrated acids), and the solution does not contain metapectic acid; that which is prepared from pectin decomposes much more quickly. When the first-mentioned pectic acid is boiled with dilute mineral acids, the liquid soon acquires a faint red colour, reduces copper- and silver-salts, and if sulphuric acid is used, gives off carbonic and formic acids, and, finally, an odour of caramel. The solution, which remains colourless if diluted at the right moment, leaves a black product when filtered, and if evaporated after the sulphuric acid has been removed by carbonate of baryta, it leaves a syrup from which alcohol precipitates a baryta-salt soluble in water, leaving in solution a sugar (partly converted into caramel), which is fermentable and capable of uniting with common salt. The baryta-salt, which is soluble in water, appears to contain formic acid, and an acid similar to malic acid. (Chodnew.)—The jelly of pippins completely freed from sugar by alcohol, is converted into sugar by 20 minutes' boiling with oxalic acid (Couverchel, *Ann. Chim. Phys.* 46, 181). According to Fremy, pectic acid is transformed by acids in the same manner as by water, therefore without formation of sugar.

5. With *nitric acid*, pectic acid yields oxalic acid (Vauquelin) and mucic acid (Braconnot). Strong nitric acid eliminates carbonic acid, and forms carbonic and mucic acids (Regnault). Chodnew obtained mucic acid from pectin, but not from pectic acid.

6. When pectic acid is heated with the aqueous solution of *caustic alkalis* or *alkaline carbonates*, metapectic acid is formed. (Fremy.) Pectin and pectic acid prepared from it undergo these transformations much more readily than ordinary pectic acid. (Fremy, Chodnew.) The liquid acquires a brown colour, but is not found to contain oxalic acid. (Fremy.) When pectic acid (from turnips) has been boiled for some time with potash-ley, the solution is not precipitated by acetic acid; but hydrochloric and nitric acids soon render it turbid, and at last throw down flakes. From the solution neutralised with acetic acid, alcohol throws down a jelly; neutral acetate of lead, a precipitate

which exhibits the composition of pectate of lead (27·08 p. c. carbon, 3·16 hydrogen, 33·94 oxygen, and 35·82 oxide of lead), and when decomposed by hydrosulphuric acid, yields a black liquid, which cannot be separated from the sulphide of lead, and when mixed with alcohol solidifies to a jelly in a few hours. These precipitates are likewise formed on adding alcohol and neutral acetate of lead to a solution of pectic acid which has been boiled for three or four days with a large excess of potash, whereas aqueous pectin, after once boiling with potash-ley, is no longer precipitated by acids. (Chodnew.) See the properties of Fremy's *Metapectic acid*, p. 411.

Fromberg's pectic acid (p. 403), after boiling for half an hour with aqueous carbonate of soda, was no longer precipitated by acetic acid; but neutral acetate of lead produced a yellow-brown precipitate, which at 140° contained 41·39 p. c. PbO, and after deduction of this, 44·8 p. c. carbon, 5·33 hydrogen, and 49·87 oxygen. Another time the solution, after an hour's boiling with carbonate of soda, or a quarter of an hour's boiling with caustic soda, still yielded a precipitate with acetic acid; but after boiling for 7 to 20 hours with carbonate of soda, or digestion for 24 hours with caustic soda, no precipitate was obtained. The latter solutions, after neutralisation with acetic acid, were likewise precipitated by chloride of barium, chloride of calcium, sulphate of copper, and neutral acetate of lead; and it was only after still longer boiling with caustic soda, that a liquid was obtained, which when neutralised with acetic acid, was not precipitated by any of the above-mentioned reagents except acetate of lead. Hence the formation of metapectic acid is preceded by that of an acid which is not precipitated by acetic acid, but is thrown down from the neutral solution by lime- or baryta-salts. (Fromberg.) In this case, parapectic acid might be formed, or the non-occurrence of the precipitates might be explained by the solubility of pectic acid in organic acids. (Kr.)

When moist pectic acid is heated with hydrate of potash, the mixture soon becomes fluid and brown, but loses its colour as soon as all the water is expelled, and then contains carbonate and oxalate of potash. (Vauquelin, Gay-Lussac.)

On the behaviour of pectic acid under the influence of ferments, according to Vauquelin, see page 358.

*Combinations.* Pectic acid separated from solutions, in which state it appears as a colourless jelly having an agreeable taste (Vauquelin), must be regarded as a hydrate. It is insoluble in cold, and nearly insoluble in boiling water. The dry acid immersed in boiling water softens and swells up slightly, but does not form a jelly. (Regnault.) See above on the decomposition of pectic acid by boiling with water.

*Older statements, perhaps relating to pectosic or impure pectic acid.* The solution of pectic acid in boiling water deposits a jelly on cooling, provided it has not been altered by continued boiling. (Vauquelin.) The anhydrous acid scarcely swells up in cold water, and dissolves but sparingly in boiling water; the acid obtained as a jelly by precipitation from alkaline solutions, dissolves more abundantly in boiling water; the filtrate is almost clear, reddens litmus very slightly, and is converted by acids, neutral salts, sugar, and alcohol, into a transparent and colourless jelly, probably because these substances render the water incapable of holding the pectic acid in solution. Baryta- and lime-water produce similar jellies by forming insoluble salts. (Braconnot, Payen.) The hot aqueous solution does not redden litmus. (Guibourt.)

*With Bases.* — Pectic acid unites with bases, forming salts, among



which only those of the alkalis are soluble in water, the rest being insoluble and gelatinous. The jellies precipitated from cold solutions are denser than those obtained from hot solutions (Regnault). At a moderate heat, the acid expels carbonic acid from alkaline carbonates. It dissolves easily in aqueous alkalis, even after drying. The solution is not precipitated by mercuric chloride, but with all other salts it yields gelatinous precipitates, which dissolve in excess of alkali.---It is difficult to obtain the salts at a definite degree of saturation, because the neutral salts formed at first take up an additional quantity of pectic acid (Regnault, Fremy). When a soluble pectate is precipitated by a metallic salt, the composition of the precipitate depends upon that of the soluble salt, and varies with it (Regnault). The jellies precipitated by metallic salts from pectate of ammonia and pectate of lime, are transparent if the acid was pure. They obstinately retain portions of the precipitant, which cannot be removed by washing on the filter, but may be got rid of by pressing the jelly with the hand, pouring fresh water upon it, and so on, whereby the salt acquires the consistence of woody fibre, and becomes friable after drying (Chodnew). The insoluble salts dry up to very hard, difficultly friable, horny, hygroscopic masses. They take fire when heated in contact with the air, retain water obstinately, so that they cannot be dried below  $140^{\circ}$  or  $150^{\circ}$ , and decompose at about  $200^{\circ}$  (Regnault).

*Pectate of Ammonia.*—The solution of pectic acid in excess of aqueous ammonia slowly turns sour on boiling, and when evaporated in vacuo, leaves a transparent mass whose aqueous solution has a slight acid reaction (Regnault).—From the solution of pectic acid in aqueous ammonia, alcohol precipitates a transparent, colourless jelly, which, at  $100^{\circ}$ , becomes red-brown and not friable, and dissolves in water, forming an acid, coloured liquid (Chodnew). The acid ammoniacal salt which remains on evaporation, swells up in water and dissolves—assimilating at the same time a considerable quantity of water—to a tasteless liquid which reddens litmus (Braconnot). Aqueous pectate of ammonia yields gelatinous precipitates with chloride of sodium, acetate of potash, and other neutral salts, also with alcohol and sugar (Braconnot; Simonin, *J. Pharm.*, 20, 478.)

*Pectate of Potash.*—When pectic acid in excess is digested with potash-ley, a large quantity of pectic acid is taken up, and a solution formed which is neutral at first, but afterwards becomes slightly acid. When a solution of pectic acid in excess of potash-ley is mixed with alcohol, a basic jelly is precipitated, from which potash is extracted by washing with alcohol (Regnault).—The potash-salt obtained by precipitating pectic acid dissolved in excess of potash-ley with alcohol, and washing out the jelly with alcohol, acquires, at  $120^{\circ}$ , the character of woody fibre, but does not become friable; between  $150^{\circ}$  and  $160^{\circ}$  it gives off water, turns yellowish-brown, and then dissolves in water to a clear liquid, which smells of caramel and reduces cupric oxide (Chodnew).—Potash, added in excess to a solution of the potash-salt, throws down a jelly, which recovers its solubility in water after the excess of potash has been removed, and, according to Braconnot, is a basic salt.

Calculation according to Chodnew.				Chodnew.	
				at 120°.	at 150°—160°.
28 C .....	168.0	...	34.25	..... 33.80	..... 35.44
20 H .....	20.0	...	4.07	..... 4.31	..... 4.02
26 O .....	208.0	...	42.44	..... 43.00	..... 40.54
2 KO .....	94.4	...	19.24	..... 18.89	..... 20.00
$C^{28}H^{20}O^{26}, 2KO$ ...				490.4	..... 100.00
				100.00	..... 100.00

At 150°—160°, =  $C^{28}H^{18}O^{24}, 2KO$  (calc. 35.56 p. c. C., 3.81 H., 40.65 O., 19.98 KO.) (Chodnew.)

*Pectate of Soda.*—Obtained like the potash-salt, which it resembles. Dissolves in water after drying at 120°. Neutral. Swells up when heated in a platinum spoon. Contains 13.73 p. c. soda, corresponding to the formula  $C^{28}H^{20}O^{26}, 2NaO$  (calc. 13.54 NaO) (Chodnew).

*Pectate of Baryta.*—Aqueous pectic acid forms a gelatinous precipitate with baryta-water (Braconnot).—When aqueous pectin is immersed in a large excess of baryta-water, in a vessel from which the air is excluded, pectosate of baryta is first precipitated and subsequently converted, by the excess of baryta, into pectate. This, after washing, drying in vacuo, and then at 120°, contains from 25.3 to 26.8 p. c. baryta, corresponding to the formula  $C^{28}H^{20}O^{26}, 2BaO$  (calc. 26.0 p. c. BaO) (Fremy).—Obtained like the lime-salt, which it resembles. The salt, dried between 150° and 160°, contains 2 at. water less than that dried at 120° (Chodnew).

Calculation according to Chodnew.				Chodnew.	
				at 120°.	at 150°—160°.
28 C .....	168	...	30.58	..... 30.50	..... 31.57
20 H .....	20	...	3.64	..... 3.69	..... 3.29
26 O .....	208	...	37.90	..... 38.13	..... 36.46
2 BaO .....	153	...	27.88	..... 27.68	..... 28.68
$C^{28}H^{20}O^{26}, 2BaO$ ...				549	..... 100.00
				100.00	..... 100.00

Calculation for the salt dried between 150° and 160°, 31.63 p. c. C., 3.38 H., 36.15 O., and 28.84 BaO =  $C^{28}H^{18}O^{24}, 2BaO$ . (Chodnew.)

*Pectate of Lime.*—Lime-water added to aqueous pectic acid, and lime-salts added to pectate of ammonia, throw down gelatinous precipitates. Pectate of ammonia is likewise decomposed by sulphate and bicarbonate of lime, but not by the neutral carbonate. From dilute solutions of alkaline pectates, a few drops of lime-water throw down gelatinous masses which are insoluble in alkalis. Pectate of lime does not dissolve in boiling water or in ammonia, and is not decomposed by potash-ley; but it is decomposed by hydrochloric acid, with separation of pectic acid, and by heated carbonate of soda, with separation of carbonate of lime (Braconnot, *Ann. Chim. Phys.* 44, 60; 47, 268).—The transparent and colourless jelly precipitated from neutral pectate of ammonia by aqueous chloride of calcium, is harder than pectic acid, and becomes yellowish after being pressed, washed, and dried at 120°. (Chodnew.)

Calculation according to Chodnew.				Chodnew. mean, at 120°.
28 C .....	168	.....	37.08	..... 36.77
20 H .....	20	.....	4.41	..... 4.65
26 O .....	208	.....	45.94	..... 46.16
2 CaO .....	56	.....	12.57	..... 12.42
$C^{28}H^{20}O^{26}, 2CaO$ ... 452				..... 100.00
				..... 100.00

Compare Mulder's analyses, p. 403.

*Pectate of Lead.* — When an aqueous solution of neutral acetate of lead is poured into an aqueous solution of pectate of ammonia having an alkaline reaction, a transparent jelly is formed, containing 48.71 p. c. oxide of lead (Regnault). The precipitate thrown down from neutral pectate of ammonia by neutral acetate of lead contains between 32.7 and 35 p. c. lead-oxide; from an ammoniacal solution of the neutral acetate, soluble pectates throw down precipitates containing as much as 60 p. c.  $PbO$ , and more in proportion as the solution is more ammoniacal (Fremy). — From cold pectic acid (pectate of ammonia?), neutral acetate of lead, throws down neutral pectate of lead containing 36.06 p. c. lead-oxide (Chodnew's formula  $C^{28}H^{20}O^{26}, 2PbO$  requires 36.13 p. c.  $PbO$ ); from the hot solution a basic salt is obtained in the form of a jelly which easily separates into flocks, and when dry becomes yellow and very friable (Chodnew). — By boiling with water, it is converted into parapectate of lead (Fremy).

Calculation according to Fremy.				Fremy.
32 C .....	192	.....	29.09	..... 28.51
20 H .....	20	.....	3.03	..... 3.17
28 O .....	224	.....	33.94	..... 35.22
2 $PbO$ .....	224	.....	33.94	..... 33.10
$C^{32}H^{20}O^{28}, 2PbO$ ... 660				..... 100.00
				..... 100.00

Calculation according to Chodnew.				Regnault.	Chodnew.
28 C .....	168	.....	23.28	..... 21.87	..... 23.06
19 H .....	19	.....	2.63	..... 2.26	..... 2.55
25 O .....	200	.....	27.72	..... 27.13	..... 28.07
3 $PbO$ .....	336	.....	46.37	..... 48.74	..... 46.32
$C^{28}H^{19}O^{25}, 3PbO$ ... 723				..... 100.00	..... 100.00
				..... 100.00	..... 100.00

Compare Mulder's analysis, p. 403.

Pectic acid protects *ferric salts* from precipitation by alkalis (H. Rose).

*Pectate of Copper.* — Pectate of potash forms with sulphate of copper a bulky coagulum, the liquid not retaining a trace of copper; the greenish precipitate is insoluble in boiling water; gives up part of its acid to potash, the residual salt not being dissolved thereby; and is decomposed by nitric but not by acetic acid (Braconnot).

A solution of sulphate of copper poured into aqueous pectate of ammonia, throws down a green jelly of variable composition, which dries up to a yellow mass (Regnault). Pectate of copper is green both before and after drying (Chodnew).

Calculation according to Chodnew.				Chodnew. at 120°.
28 C .....	168	.....	35.34	..... 35.09
20 H .....	20	.....	4.19	..... 4.21
26 O .....	208	.....	43.79	..... 43.84
2 CuO.....	80	.....	16.68	..... 16.86
$C^{28}H^{20}O^{26}, 2CuO$ .....				476 ..... 100.00 ..... 100.00

For Mulder's and Fromberg's results, see page 403.

The precipitate formed by sulphate of copper in ammoniacal pectate of ammonia, continues to redissolve for a long time, till finally a blue ammoniacal jelly is precipitated, probably a double salt. (Regnault.)

*Pectate of Silver.*—Obtained by double decomposition of pectate of ammonia with nitrate of silver, and contains an amount of oxide of silver varying with the constitution of the pectate of ammonia used. *a.* When nitrate of silver is poured into aqueous pectate of ammonia which has been boiled as long as ammonia continues to escape, a precipitate is formed containing 38.38 p. c. AgO. — *b.* When aqueous pectate of ammonia is poured into nitrate of silver, the precipitate contains 36.95 p. c. AgO. — *c.* When pectate of ammonia is prepared by evaporation in vacuo, and nitrate of silver is poured into its aqueous solution, the precipitate contains 40.39 and 41.02 p. c. AgO. — *d.* When nitrate of silver is poured into pectate of ammonia containing excess of ammonia, the resulting precipitate continues for a long time to redissolve, and when it no longer disappears on stirring, contains 38.48 and 36.68 p. c. AgO (Regnault).

Neutral pectate of silver is obtained by precipitating pectate of ammonia with nitrate of silver; but if the nitrate of silver has any free acid adhering to it, the precipitated pectate of silver is mixed with pectic acid and therefore exhibits a smaller amount of silver-oxide (Chodnew).

Calculation according to Fremy.				Calculation according to Chodnew.			
32 C .....	192	...	28.74	28 C .....	168	...	26.75
20 H .....	20	...	2.99	20 H .....	20	...	3.18
28 O .....	224	...	33.53	26 O .....	208	...	33.15
2 AgO .....	232	...	34.74	2 AgO .....	232	...	36.92
$C^{32}H^{20}O^{28}, 2AgO$ ....				$C^{28}H^{20}O^{26}, 2AgO$ .....			
668				628			
100.00				100.00			

		Regnault.		Fremy.		Chodnew. at 100°.	
	<i>a.</i>		<i>c.</i>				
C .....	26.41	...	25.29 and 25.87	.....	27.07	.....	26.45
H.....	2.79	...	2.74 „ 2.80	.....	3.33	.....	3.10
O .....	32.42	...	30.95 „ 30.94	.....	32.81	.....	33.75
AgO.....	38.38	...	41.02 „ 40.39	.....	36.79	.....	36.70
100.00		...	100.00 „ 100.00	.....	100.00	.....	100.00

Fremy's analysis (*J. Pharm.* 26, 379) does not agree with his later formulæ; moreover he does not quote it any more. The calculation is deduced from his formula of pectic acid and the other pectates.

*With Salts.*—Pectic acid dissolves in aqueous solutions of the neutral salts, especially the ammonia-salts, of many organic acids. When small quantities of citrate or malate of ammonia, or other similar salt, is added to water in which pectic acid is suspended, an acid

solution is produced from which alcohol throws down a jelly which dissolves in boiling water, and separates again on cooling. This jelly is a compound of pectic acid with an ammonia-salt; it is decomposed by prolonged boiling, or by repeated precipitation with alcohol and re-solution in water, and is thereby rendered partially insoluble in water. Such compounds are obtained by boiling carrot-pulp with acids, provided the pulp has not been previously exhausted with acids,—and may be confounded with pectin (Fremy). Chodnew's pectous acid (p. 396), might therefore belong to this place. (Kr.)

Pectic acid is insoluble in *alcohol* and in *ether*.—In aqueous organic acids it does not dissolve more freely than in pure water. (Braconnot, *Ann. Chim. Phys.* 50, 382.)

### Parapectic Acid.

(<sup>24</sup>||<sup>17</sup>)<sup>23</sup>?

FREMY. *N. Ann. Chim. Phys.* 24, 34.

Resembles metapeptic acid in being soluble in water, but is distinguished therefrom by forming a precipitate with baryta-water. See page 398.

When pectic acid is boiled for some time with water, it dissolves as parapectic acid. In like manner, pectates heated for several hours to 150° or boiled with water, are converted into parapectates.

Parapectic acid is uncrystallizable, destitute of optical rotatory power, and has a strong acid reaction. When *heated*, it behaves like pectin; when dissolved in *water*, it is quickly converted into metapeptic acid; when boiled with *potassio-cupric tartrate*, it precipitates cuprous oxide; and it is not fermentable.—It forms soluble salts with the *alkalis*, and is precipitated therefrom by excess of *baryta-water*; from its aqueous solution it is precipitated by alcohol. The potash-salt precipitated from its aqueous solution by alcohol and dried at 150°, contains 23 p. c. potash ( $C^{24}H^{15}O^{21}, 2KO = 22.4$  p. c. KO).—The *lead-salt* is obtained by boiling pectate of lead suspended in water for several hours, or by precipitating aqueous parapectic acid with neutral acetate of lead.

<i>Lead-salt at 150°.</i>				Fremy.	
24 C .....	144.0	.....	26.16	.....	25.04
15 H .....	15.0	.....	2.72	.....	2.68
21 O .....	168.0	.....	30.54	.....	31.57
2 PbO .....	223.4	.....	40.58	.....	40.71
$C^{24}H^{15}O^{21}, 2PbO$ .....				550.4	..... 100.00
				100.00	..... 100.00

At 110° it contains 24.44 p. c. C., and 2.92 H.; therefore 2 at. water more. (Fremy.)

## Metapectic Acid.

?  $C^8H^7O^9$  or  $C^{16}H^{14}O^{18}$ .

FREMY. *J. Pharm.* 26, 382; *Ann. Pharm.* 35, 322; *J. pr. Chem.* 22, 1. — *N. Ann. Chim. Phys.* 24, 36; *Ann. Pharm.* 67, 288; *J. pr. Chem.* 45, 412. — *Compt. rend.* 48, 202; *N. J. Pharm.* 35, 81; abstr. *Rép. Chim. pure*, 1, 269. — *Compt. rend.* 49, 561; *Rép. Chim. pure*, 1, 602; *Chem. Centr.* 1860, 4. — *Kopp's Jahresber.* 1859, 530 and 540.

*Acide cellulosique.* — Occurs as a product of the transformation of pectose, in all fluids of the vegetable organism which are in contact with tissue containing pectose.

*Formation.* All pectous substances may be converted either directly into metapectic acid, or into products which yield this acid after further treatment (pp. 397, 398.) — When lime is allowed to act on mangold-wurzel pulp in the manufacture of sugar on the large scale, metapectate of lime may be formed, which then accumulates in the molasses.

*Preparation.* Clopped mangold-wurzel is washed with water; the residue is boiled for an hour with milk of lime and pressed; and the liquid is evaporated to a syrup and mixed with alcohol. Metapectate of lime then falls to the bottom, and after it has been decomposed by oxalate of ammonia, the filtered solution is mixed with excess of neutral acetate of lead to precipitate colouring matter, phosphoric acid and other substances; and the filtrate is supersaturated with ammonia, which throws down metapectate of lead. By decomposing this salt under water with hydrosulphuric acid and evaporating the filtrate, aqueous metapectic acid is obtained.

*Properties.* Amorphous, strongly acid mass, destitute of rotatory power.

*Decompositions.* 1. When heated, it behaves like pectin (p. 396). — 2. The aqueous solution quickly becomes covered with mould, and is decomposed by prolonged boiling, with formation of acetic acid and black ulmic acid. — 3. It reduces *potassio-cupric tartrate* at the boiling heat. — 4. It reduces aqueous *silver-* and *gold-salts*.

Metapectic acid is deliquescent and dissolves readily in water. — The *metapectates* (excepting the basic salts) are all soluble in water. The aqueous acid decomposes carbonates and neutralises strong bases.

*Metapectate of Lead.* — Aqueous metapectic acid precipitates basic acetate of lead, but not the neutral acetate. The aqueous solutions of the alkaline metapectates added to neutral or basic acetate of lead in excess (of the lead salt?) throw down soluble precipitates. — The precipitates thrown down from aqueous metapectic acid by basic acetate of lead contain from 67.5 to 68.8 p. c. ( $C^8H^5O^7, 2PbO = 67.2$  p. c.  $PbO$ ) and 73.4 to 74.2 p. c. oxide of lead ( $C^8H^5O^7, 3PbO = 75.4$  p. c.  $PbO$ ); after deduction of the lead-oxide, they contain, on the average 43.51 p. c. C., 4.58 H., and 51.91 O., corresponding to the formula  $C^8H^5O^7$ , (calc. 44.08 p. c. C., 4.58 H., and 51.34 O.). Fremy formerly analysed lead-salts containing smaller quantities of lead-oxide (40.9 and 46.73 p. c.).

## Jelly from Yellow Pods.

v. ORTH. *Wien. Akad. Ber.* 13, 512; *J. pr. Chem.* 64, 10.  
L. MAYER. *Wien. Akad. Ber.* 20, 529; *J. pr. Chem.* 69, 215.

Occurs in the fruit of *Gardenia grandiflora*.—The yellow pods, after being exhausted with alcohol of 40°, are boiled with water; the filtrate, after addition of hydrochloric acid, is precipitated with alcohol; and the solution in water acidulated with hydrochloric acid, and precipitation with alcohol, are repeated as long as the precipitate appears coloured.

Calculation according to v. Orth.				v. Orth. at 100°.
32 C .....	192 .....	42.10 .....		42.04
24 H .....	24 .....	5.26 .....		5.36
30 O .....	240 .....	52.64 .....		52.60
<hr/>				
C <sup>32</sup> H <sup>24</sup> O <sup>30</sup> .....	456 .....	100.00 .....		100.00
<hr/>				
Calculation according to Mayer.				Mayer. mean.
64 C .....	384 .....	41.07 .....		40.90
47 H .....	47 .....	5.03 .....		5.33
63 O .....	504 .....	53.90 .....		53.77
<hr/>				
C <sup>64</sup> H <sup>47</sup> O <sup>63</sup> .....	935 .....	100.00 .....		100.00

After deduction of 1.8 and 0.79 p. c. ash.—It may perhaps be isomeric or identical with parapectin (p. 399). Kr.

When heated with *hydrochloric acid*, it behaves in the same manner as jelly from *Syringa*.

Jelly from *Syringa*.

v. PAYR. *Wien. Akad. Ber.* 20, 527; *J. pr. Chem.* 69, 213.

Occurs in the fruit of *Syringa vulgaris*.—The fruits separated from the stalks are boiled for a few minutes with water, and the liquid, after being strained, is precipitated with neutral acetate of lead. The dirty brown precipitate, diffused in water after washing, dissolves partially on addition of acetic acid. On decomposing the undissolved part under water with hydrosulphuric acid, separating the sulphide of lead, concentrating the filtrate, decolorising with animal charcoal, adding hydrochloric acid and precipitating with alcohol, a transparent jelly is obtained which may be decolorised by repeated solution in water containing hydrochloric acid, and precipitation with alcohol.

Calculation according to v. Payr.				v. Payr. mean.
64 C .....	384 .....	41.47 .....		41.4
46 H .....	46 .....	4.97 .....		5.2
62 O .....	496 .....	53.56 .....		53.4
<hr/>				
C <sup>64</sup> H <sup>46</sup> O <sup>62</sup> .....	926 .....	100.00 .....		100.0

After deduction at 2.8 p. c. ash. — Isomeric with parapectin (p. 399).

The aqueous solution heated to 100° for several hours with *hydrochloric acid*, deposits on cooling a white powder which at 100° contains 39·81 p. c. carbon, 5·24 hydrogen, and 54·95 oxygen, corresponding therefore to the formula  $C^{64}H^{50}O^{66}$  (calc. 39·92 p. c. C., 5·20 H. and 54·88 O), and is formed by assumption of 4 at. water. (v. Payr.)

### Sacc's Pectic Acid from Wood.

SACC. *N. Ann. Chim. Phys.* 25, 218; *J. pr. Chem.* 46, 430; abstr. *Pharm. Centr.* 1849, 235; *Chem. Gaz.* 1849, 274.

PORTER. *Ann. Pharm.* 71, 115; abstr. *Pharm. Centr.* 1849, 777; *Chem. Gaz.* 1849, 469.

The substance produced by boiling wood with nitric acid (from the incrusting matter, p. 124, according to Sacc), consists, according to Sacc, of pectic acid; according to Porter, it is a different body.

Sacc boils deal-shavings for some hours with 2 pts. water and 10 pts. commercial nitric acid, whereupon reddish vapours are at first abundantly evolved, and the wood is converted into a white doughy mass. This he washes with water to remove all the acid, then collects it on linen, and dries it over the water-bath.—Porter further treats the mass thus obtained with dilute aqueous ammonia, which leaves a portion undissolved and precipitates the filtrate with hydrochloric acid.

Light grey (Sacc), or reddish grey (Porter), easily friable mass.

Calculation according to Porter.				Sacc.		Porter. mean.	
16 C .....	96	....	43·63	.....	40·83 to 42·86	.....	43·39
12 H .....	12	....	5·45	.....	5·86 „ 5·94	.....	5·86
14 O .....	112	....	50·92	.....	53·31 „ 51·20	.....	50·75
$C^{16}H^{12}O^{14}$ ....	220	....	100·00	.....	100·00 100·00	.....	100·00

After deduction of  $\frac{1}{4}$  to  $\frac{1}{2}$  p. c. ash. Sacc gives the formula  $C^{16}H^{12}O^{13}$  which he regards as that of pectic acid.

*Decompositions.* 1. When heated, it chars quickly without detonation, emitting an odour of caramel and leaving charcoal (Sacc).—2. By boiling with moderately dilute *nitric acid*, it is converted into oxalic acid, without formation of mucic acid. —3. With *oil of vitriol*, it chars and gives off an odour of caramel (Porter).—4. *Hydrochloric acid* at the boiling heat colours it red. After boiling for some time with aqueous *alkalis*, it is no longer precipitable by acids (Porter).

It does not dissolve in *water* either cold or boiling. — When newly prepared and moist, it dissolves easily in water containing *ammonia*, and is precipitated therefrom by weak acids, as a stiff, colourless, transparent jelly. After drying, it is insoluble in aqueous ammonia (Sacc). It dissolves with difficulty in aqueous *alkalis*, and is thrown down by acids from concentrated solutions as a white light powder; from more dilute solutions, as a transparent precipitate, which quickly unites in white flocks. Alcohol and metallic salts likewise precipitate



the alkaline solution. The last formed precipitates have the aspect of pectates (Porter).

*Glucosides or Conjugated Compounds of the Saccharoïd Substances.*

**Chitin.**



- ODIER (1823). *Mém. Soc. d'hist. natur. de Paris*, 1, 29; *N. Tr.* 8, 1, 233; *Mag. Pharm.* 5, 301; *J. Pharm.* 9, 379; *Berz. Jahresber.* 4, 247.
- LISSAIGNE. *Compt. rend.* 16, 1087; *J. Chim. mèd.* 19, 379; *J. pr. Chem.* 29, 323; *Berz. Jahresber.* 24, 699.
- PAYEN. *Compt. rend.* 17, 227; *Berz. Jahresber.* 24, 709.
- K. SCHMIDT. *Ann. Pharm.* 54, 298.
- SCHLOSSBERGER. *Ann. Pharm.* 98, 99; *N. Jahrb. Pharm.* 5, 297; *abstr. J. pr. Chem.* 68, 162; *Chem. Centr.* 1856, 487.
- BERTHELOT. *Compt. rend.* 47, 227; *J. pr. Chim.* 76, 371; *Chem. Centr.* 1856, 676; *Rép. Chim. pure* 1, 69; in detail: *N. Ann. Chim. Phys.* 56, 149.
- PELIGOT. *Compt. rend.* 47, 1034; *N. Ann. Chim. Phys.* 58, 83; *Rép. Chim. pure*, 1, 234; *Chem. Centr.* 1859, 709; *Zeitschr. Pharm.* 3, 241.
- STÄDELER. *Ann. Pharm.* 111, 21; *Chem. Centr.* 1859, 708.

*Endomaderm* (Lassaigne). — Discovered and distinguished from horn-substance by Odier, in 1821; recognised as a nitrogenous compound by Lassaigne; first more completely investigated by K. Schmidt. Fremy's non-azotised chitin is essentially distinguished from that of all other chemists by the absence of nitrogen. Peligot's chitin appears (according to Städeler) to have contained cellulose derived from remains of leaves. — Peligot regards chitin in general as a compound of cellulose with protein-substances.

*Occurrence.* Chitin forms the chief constituent of the envelopes, scales and hairs of articulated animals, also of the lining membranes of the trachea and intestines (*Handb.* viii, *Zoochem.* 462). Many tissues designated by histologists as chitin, agree with that substance only in their behaviour with potash-ley and acetic acid, and have not been shown to be identical with it. Thus the byssus of acéphale contains, not chitin as supposed by Leuckart (*Wegm. Arch.* 1852, 25), but a substance richer in nitrogen (see *Conchiolin*); muscle-shells contain, not chitin [contrary to the statement of Kuss (*Dissertation über Structur und Zusammensetzung der Muschelschalen*, 1853)], but conchiolin (Schlossberger).

*Preparation.* The tissues intended for the preparation (carapaces of the crab, wing-cases of the cockchafer, and similar material) are deprived, by successive treatment with water, alcohol, dilute acids, potash-ley and ether, of all matters soluble in these liquids, and the residue is then washed and dried. If tissues are used likewise containing tunica or cellulose, or if entire animals having remains of leaves in their intestines, are subjected to the same treatment, the chitin will be contaminated with these substances. When chitin thus prepared is boiled for 12 hours or longer with a mixture of 1 vol. oil of vitriol and 4 vol. water, part of it is converted into

soluble products; but the residue, which swells up to a pasty mass, is perfectly pure chitin (free from ash) which may be washed by decantation, so long as it contains free acid, but as soon as all the acid is removed, remains partly suspended in the liquid, and can only be recovered by evaporating the water (Städeler).

If the skin of silk-worms be treated successively with potash-ley, alcohol, ether, and acetic acid, the residual chitin contains 48.13 p. c. C., 8.30 N., 6.90 H., and 36.67 O.; after further treatment with permanganate of potash, 47.38 p. c. C., 6.15 N., 7.02 H., and 39.45 O. When silk-worms are boiled with strong potash-ley, which disintegrates or dissolves their several organs as well as the remains of leaves in their intestines, then with dilute sulphuric acid, and the skins, which remain as translucent bags open at both ends, are washed, dried and treated with sulphuric acid containing 6 at. water, they lose 44 p. c. of their weight, but the residue still contains 5.8 p. c. nitrogen. If they are then treated for several hours with hot, or for some days with cold concentrated aqueous permanganate of potash, then with bisulphite or potash, and finally with water, there remains a white, interlaced mass which does not give off ammonia when boiled with potash. This mass, however, if made up into a paste with hydrate of potash and water, and heated to 100° for eight days, dissolves with evolution of ammonia, and forms a soap, from which, after filtration, acids separate fatty acids; but even after two-thirds of the whole has been decomposed, the rest of the chitin still contains 6.2 p. c. nitrogen, and continues to evolve ammonia. When this chitin, after being softened in water, is treated with oil of vitriol and iodine, it exhibits under the microscope, numerous brown integuments and isolated irregular particles which are coloured blue. The latter colouring becomes more plainly visible, if the skin is left for some days in the iodine-solution and then moistened with oil of vitriol, whereupon pieces of membrane make their appearance, greenish at first, but changing to indigo-blue as the iodine evaporates. From this chitin, aqueous cuprammonia extracts cellulose which is precipitated from the solution by acids. The horny substance of the lobster likewise exhibits the reaction of cellulose (p. 137) with oil of vitriol and iodine. (Peligot.) This chitin is rightly regarded by Städeler as impure; from pure chitin he was unable to extract anything by cuprammonia.

*Fremy's Chitin.* — When the skeletons of crustacea are treated with cold dilute hydrochloric acid, the undissolved residue is boiled for several hours with potash-ley and again washed with water, alcohol and ether, a transparent horny substance is obtained, containing on the average 43.35 p. c. C., 6.65 H., and 50.00 O., but no nitrogen, and therefore isomeric with cellulose ( $C^{12}H^{10}O^{10}$ ). This substance is not altered by dilute acids or alkalis, and not converted either into sugar by the former, or into pyroxylin by fuming nitric acid, which indeed has no action on it whatever. By concentrated acids, it is disintegrated, dissolved, and converted into an acid comparable with metapeptic acid (p. 411); by boiling nitric acid it is converted into oxalic acid (Fremy, *N. Ann. Chim. Phys.* 43, 93).

*Properties.* White amorphous mass, which, when examined with the microscope, often exhibits the structure of the tissues from which it has been prepared. — Chitin which has been boiled for a long time with dilute sulphuric acid, and separated by evaporating the water in

which it was suspended, forms hard, transparent or translucent, coherent films, which are extremely difficult to comminute (Städeler).

				Schmidt. <i>mean.</i>	Lehmann. <i>mem.</i>	Städeler.
18 C	108	...	46.35	...	46.71	46.73
N	14	...	6.01	...	6.50	6.49
15 H	15	...	6.44	...	6.82	6.59
12 O	96	...	41.20	...	39.97	40.19
$C^{18}NH^{15}O^{12}$	233	...	100.00	...	100.00	100.00

Schmidt's chitin mostly contained ash to the amount of 2 per cent. — Payen found 8.99 p. c. nitrogen, Schlossberger 6.4 p. c. See the analysis by Children & Daniell (*Handb.* viii, *Zoochem.* 470). Respecting Peligot's analysis and Fremy's chitin (p. 415). — Schmidt gave the formula  $C^{17}NH^{14}O^{11}$ ; Städeler that which is here adopted. — Free from sulphur and phosphorus. (Schmidt.)

*Decompositions.* 1. Chitin chars when heated, but neither melts nor changes in form, and does not yield any carbonate of ammonia. (Odier.) By destructive distillation, water, acetic acid, acetate of ammonia and a small quantity of empyreumatic oil are obtained, while charcoal is left retaining the original form of the chitin. (Schmidt.) — 2. Chitin which had been kept under water for a year, was partly dissolved and partly changed into a slimy mass. (Schlossberger.) The skin of silk-worms, where freed by means of water and alcohol from all adhering substances, is not perceptibly altered by long boiling with water; the water takes up, however, a small quantity of a nitrogenous substance which, when the solution has been evaporated to a small bulk, is precipitable by tannic acid, chlorine, or alcohol. It thus appears that gelatin is hereby formed from the skins. (Lassaigne.) Chitin, heated to 280° with water in a sealed tube, becomes brown and brittle, but is not dissolved or otherwise altered. (Schmidt.) — 3. Chitin dissolves in warm oil of vitriol. (Odier.) Oil of vitriol with  $1\frac{1}{2}$  at. water disintegrates and immediately dissolves it; oil of vitriol with 3 at. water disintegrates it after some hours. (Payen.) When immersed in oil of vitriol, it becomes transparent, melts at the edges, and is completely dissolved after a quarter of an hour. (Schlossberger.) It swells up in oil of vitriol and dissolves without coloration; the solution becomes coloured on standing, and after 48 hours it is black, has deposited a small quantity of insoluble matter, has a choking smell, and contains acetic acid and an ammonia-salt. (Schmidt.) The colourless solution of chitin in cold oil of vitriol is not precipitated by water after a few hours; but on neutralising it with carbonate of baryta, a soluble baryta-salt is obtained, while the solution immediately reduces potassio-cupric tartrate. (Städeler.) — When chitin is diffused in oil of vitriol and the solution dropped into 100 times its own weight of water, then boiled for an hour and afterwards neutralised with chalk, sugar is obtained on evaporation. On the kind of sugar see p. 342. (Berthelot.) When chitin is boiled with moderately dilute sulphuric acid, as described at page 415, the undissolved and undecomposed portion being removed, the acid solution evolves ammonia when supersaturated with lime, and, after evaporation of the filtrate to a syrup, amorphous sugar remains which easily reduces cupric tartrate. No tyrosine, leucine or glyccol accompanies the sugar, but it contains a small quantity of an amorphous substance. (Städeler.) See Städeler's equation for this decom-

position, p. 342). — 4. Chitin dissolves in concentrated *hydrochloric acid* without change of colour. (Schmidt.) The skins of insects when immersed in hydrochloric acid containing 6 at. water, become transparent, are disintegrated, and, after a few minutes, dissolved. After neutralisation of the solution by alkalis, tannic acid throws down a precipitate containing nitrogen. (Payen.) — Chitin may be bleached by *chloride of potash* or of *soda*. (Lassaigne.) A cold, saturated aqueous solution of *chloride of lime* quickly destroys the skins of insects (Payen).

5. Chitin is coloured orange-yellow by *solution of iodine* (dark brown-red by iodine-water: *Städeler*); addition of oil of vitriol occasions disintegration, but neither violet nor blue coloration. (Payen. — See the statements of Peligot, p. 415, and those of Rouget, below.) — 6. Chitin is not coloured by *nitric acid*, but quickly dissolved. (Odier, Lassaigne.) It dissolves in concentrated nitric acid without change of colour (Schmidt), in an equal quantity of cold nitric acid with 4 at. water. (Payen.) — Crabs' claws immersed in nitric acid, become transparent after a few moments; if the acid is drained off, the membrane retains at first its original form, but afterwards deliquesces to a colourless liquid, beginning at the edges. (Payen.) — 7. Chitin is not altered by ebullition with *potash-ley* (Odier), or when heated with a solution of 1 pt. potash-hydrate in 3 pts. water. (Lassaigne.) It remains unchanged when heated for days with very concentrated solution of potash, and when heated with potash-ley to 210° in a sealed tube, it behaves as when it is heated with water. (Schmidt.) When fused with solid hydrate of potash, it evolves ammonia without charring, leaving a residue which is soluble in water. (Payen.) The membranous tissue of the articulata, either in its original condition or when the incrustations have been dissolved by hydrochloric acid, gives the rose-red coloration, characteristic of the nitrogenous tissues, when treated with mercuric nitrate, and the orange-red coloration with nitric acid and ammonia, but with iodo-chloride of zinc (p. 140) it is coloured uniformly violet. After ebullition with potash-ley of 40°, whereby it remains unaltered as to external appearance and as to its appearance under the microscope, it more quickly assumes an intenser bluish violet colour when treated with iodo-chloride of zinc; it still, however, remains unattackable by concentrated potash-ley, acetic or tartaric acid. — If chitin is boiled for half an hour with 5 times its weight of potash-hydrate and such a quantity of water that the mixture would immediately solidify if allowed to cool, a large quantity of ammonia is liberated, and half the chitin is dissolved. The residue appears unchanged when examined under the microscope; it is transparent, gelatinous and easily comminuted when moist; in the dry state, it is dull-white, very light, and micaceous. With tincture of iodine, or with iodine and dilute acetic acid, this residue becomes violet throughout; iodo-chloride of zinc colours it pure blue. It dissolves almost instantly in acetic acid, tartaric acid, or in warm water containing 0.5 p. c. hydrochloric or nitric acid, and is precipitated from these solutions by alcohol or by aqueous alkalis as a semi-transparent paste, which dries up to a yellowish, translucent gum. The acid solution and the precipitate are coloured reddish violet by a few drops of biniodide of potassium. This substance, Rouget's modified chitin, dissolves in oil of vitriol with yellow or brown colour, and is precipitated by water, from the freshly prepared solution, as a white powder. The

solution is less completely precipitated by water after having been left to itself for 12 or 24 hours, and is then found to contain sugar. This modified chitin remains soluble in acids after being precipitated by alcohol or by alkalis, and still contains nitrogen. (Rouget, *Compt. rend.* 48, 703. — See also Peligot's statements, p. 415.)

Chitin is insoluble in water, aqueous ammonia, acetic acid, and alcohol. — Aqueous cuprammonia does not attack it in the smallest degree. (Städeler.)

### Myronic Acid.



LUDWIG & LANGE. *Zeitschr. Ch. Pharm.* 3, 430 and 577.

*Myronsäure.* See x, 53, also p. 316 of this volume. — Recognised as a glucoside by Ludwig & Lange, its very existence having been previously called in question by Thielau (*Pharm. Viertelj.* 7, 161) and others. Scarcely known except in the form of potash-salt.

*Preparation of Myronate of Potash.*—Vol. x, p. 53. One pound of black mustard yields from 1 to 3.5 grms. of crystals.

*Properties of the Potash-salt.*—Colourless needles, possessing a cooling, bitter taste. Neutral. Scarcely loses weight at 100°.

#### a. Calculation according to Ludwig & Lange.

20 C .....	120	.....	29.40
N .....	14	.....	3.43
19 H .....	19	.....	4.65
4 S .....	64	.....	15.68
18 O .....	144	.....	35.28
KO .....	47.2	.....	11.56
<hr/>			
$\text{C}^{20}\text{NH}^{19}\text{S}^4\text{O}^{18}, \text{KO}$ .....	408.2	.....	100.00

#### b. Calculation according to Will & Körner. Ludwig & Lange. at 100°.

20 C .....	120	.....	28.00	.....	29.98
N .....	14	.....	3.37	.....	3.97
18 H .....	18	.....	4.33	.....	4.91
4 S .....	64	.....	15.41	.....	14.93
19 O .....	152	.....	36.63	.....	34.92
KO .....	47.2	.....	11.36	.....	11.29
<hr/>					
$\text{C}^{20}\text{NH}^{18}\text{KS}^4\text{O}^{20}$ ....	415.2	.....	100.00	.....	100.00

The salt used for analysis contained about 1 p. c. of lime for which an equivalent quantity of potash was substituted in calculating the results. — Will & Körner (*Ann. Pharm.* 119, 376) give, without further details, the formula *b*, which contains the elements of glucose, oil of mustard, and acid sulphate of potash.

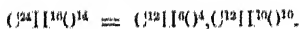
*Decompositions of the Potash-salt.*—1. When heated, it burns with a choking smell, leaving sulphate of potash and charcoal. — 2. Charred when heated with concentrated phosphoric acid, and evolves a smell of

garlic. — 3. Myronate of potash, boiled with dilute *sulphuric acid*, yields a liquid which does not ferment after neutralisation of the acid, but reduces cuprous oxide from alkaline cupric solutions. — 4. Decomposed by aqueous *ammonia*, with formation of sulphuric acid. — 5. Becomes yellow when boiled with *potash-ley*, evolves ammonia, and, after addition of hydrochloric acid, gives off hydrosulphuric acid, while a sugar which reduces alkaline cupric solutions, remains dissolved. — 6. A solution, mixed with *baryta-water* becomes turbid on boiling, from separation of sulphate of baryta, and evolves ammonia; after addition of hydrochloric acid, it evolves hydrosulphuric and carbonic acids. *Lime-water* acts like baryta-water. — 7. With *protochloride of tin*, it forms hydrosulphuric acid and protosulphide of tin. — 8. Throws down white precipitates from *neutral* and from *basic acetate of lead*, on boiling. — 9. Its aqueous solution is coloured brown-red when boiled with *ferric chloride*, and, on addition of nitric acid and chloride of barium, deposits sulphate of baryta and loses its colour. — 10. Reduces *mercurous nitrate* to the metallic state on standing, and *mercuric chloride* to calomel when heated. — 11. The solution mixed with aqueous *nitrate of silver* remains clear at first, but after a few minutes, yields a white precipitate, which dissolves when heated, the smell of oil of mustard being then evolved, and sulphide of silver deposited. — 12. It renders the colour of *bichloride of platinum* darker on boiling, and separates brown flocks from *terchloride of gold*. — 13. In contact with water and *myrosin* (x. 54), at the common temperature, it splits up, without evolution of gas, forming oil of mustard and sugar: thus, according to Ludwig & Lange:



The liquid which remains, after distilling off the oil of mustard, is acid, has a milky turbidity caused by separated sulphur, and contains  $\frac{1}{2}$  of the sulphur of the myronate of potash as sulphate of potash. With yeast it evolves a quantity of carbonic acid corresponding to as much glucose as would amount to 20.45 p. c. of the myronate of potash; but, after ebullition with dilute sulphuric acid, it evolves more, so that altogether glucose amounting to 45 p. c. of the salt is indicated. In a second experiment, less energetic myrosin formed only 18.9 p. c. glucose; in a third experiment, hardly any. — 14. *Beer-yeast* does not cause myronate of potash to ferment. (Ludwig & Lange.)

### Arbutin.



- KAWALIER. *Wien. Akad. Ber.* 9, 291; *J. pr. Chem.* 58, 193; *Ann. Pharm.* 84, 356; *Pharm. Centr.* 1852, 761; *Chem. Gaz.* 1853, 61.  
 -- Announcement of the results, *Ann. Pharm.* 82, 241.  
 AD. STRECKER. *Münch. Akad. Ber. Nr.* 69; *Ann. Pharm.* 107, 228; *N. Ann. Chim. Phys.* 54, 314; *Rép. Chim. pure*, 1, 67. — *Ann. Pharm.* 118, 292; *Rép. Chim. pure*, 4, 77.

*Occurrence.* In the leaves of *Arctostaphylos Uva Ursi*.

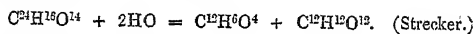
*Preparation.* The extract of the leaves is precipitated with basic acetate of lead, and the filtrate, freed from lead by sulphuretted hydrogen, is evaporated to crystallisation. The crystals are purified by recrystallisation with help of animal charcoal. (Strecker.) Kawalier precipitates the extract with sugar of lead, boils down the filtrate in a retort, removes any lead-salt which has separated, and passes hydrosulphuric acid into the liquid. The solution filtered from the sulphide of lead is evaporated to a syrup, and the arbutin, which crystallises out after several days, is purified by pressure and recrystallisation with animal charcoal.

*Properties.* See hydrated arbutin. Hydrated arbutin loses water at  $100^{\circ}$  (1 at. : Strecker), without becoming opaque, and is converted into anhydrous arbutin. Tastes bitter. Melts at a high temperature (at  $170^{\circ}$  : Strecker) to a clear, colourless liquid, which solidifies on cooling, to an amorphous cracked mass. (Kawalier.)—Neutral.

<i>at 100°, or fused.</i>				Kawalier. <i>mean.</i>	Strecker. <i>mean.</i>
24 C .....	144	...	52.94	.... 52.46	..... 52.8
16 H .....	16	...	5.88	.... 6.11	..... 5.9
14 O .....	112	...	41.18	.... 41.43	..... 41.3
<hr/>					
C <sup>24</sup> H <sup>16</sup> O <sup>14</sup> ....	272	...	100.00	.... 100.00	..... 100.0

Kawalier formerly gave the formula  $C^{32}H^{22}O^{19}$ .

*Decompositions.* 1. In contact with *emulsin* at the common temperature, it splits up after several days into hydrokinone (Kawalier's *arctuin*) and glucose. (Kawalier.)



Ebullition with dilute *sulphuric acid* has the same effect. (Strecker.) The hydrokinone may be extracted by ether from the mixture left on evaporation (Kawalier), or from the solution after ebullition with dilute sulphuric acid. (Strecker.)—2. Easily converted into kinone and formic acid by *peroxide of manganese and sulphuric acid*. (Strecker.)—3. Becomes yellow or red when *chlorine* is passed into its aqueous solution, and deposits shining yellow crystals of chlorokinone, bichlorokinone, and perhaps products still richer in chlorine. *Bromine* forms partly liquid, oily bromokinone, partly crystallised bromarbutin. (Strecker.)—4. Dissolves easily in concentrated *nitric acid*, forming a yellow solution which does not deposit crystals when evaporated, but yields a precipitate of binitrohydrokinone when mixed with alcohol. (Strecker.)

*Combinations.*—*With Water.*—A. *Hydrated Arbutin.* Long, colourless bunches of needles of a silky lustre, which lose their water at  $100^{\circ}$ .

	<i>Air-dried.</i>			Kawalier.	Strecker.	
24 C .....	144	....	51.24	....	49.93 .....	51.0
17 H .....	17	....	6.05	....	6.32 .....	6.3
15 O .....	120	....	42.71	....	43.75 .....	42.7
<hr/>						
C <sup>24</sup> H <sup>16</sup> O <sup>14</sup> + Aq.....	281	....	100.00	....	100.00 .....	100.0

B. *Aqueous Arbutin*.—Arbutin dissolves very easily in boiling water; less easily in cold water. (Strecker.)

Arbutin is not precipitated by *metallic salts*; at least not by *basic* or *neutral acetate of lead*, or by *ferric salts*. (Kawalier.) When mixed with *cupric sulphate* and excess of potash-hydrate, it forms a deep-blue solution, from which no cuprous oxide is precipitated on boiling. (Strecker.)

Arbutin is soluble in *alcohol* and in *ether*. (Kawalier.) Scarcely soluble in ether. (Strecker.)

### *Appendix to Arbutin.*

#### 1. Binitro-arbutin.



AD. STRECKER. *Ann. Pharm.* 118, 292; *Rép. Chim. pure*, 4, 77.

Arbutin is dissolved in concentrated nitric acid, and the solution is mixed with several times its bulk of alcohol. When the mixture is left to itself, needles separate out, their quantity increasing as the liquid evaporates, so that at last the mother-liquor dries up to a dark-yellow amorphous mass, from which binitro-arbutin can still be obtained by neutralisation with carbonate of baryta, and extraction with boiling alcohol.

Bright yellow, thin needles, which melt when heated and solidify in the crystalline form. Loses 9.35 p. c. water at 100° (calcul. : 4 at = 9.0 p. c.)

	at 100°.		Strecker. mean.	
24 C .....	144	39.77	39.8	
14 H .....	14	3.86	4.1	
2 N .....	28	7.74	8.2	
22 O .....	176	48.63	47.9	
<hr/>				
$\text{C}^{24}\text{X}^2\text{H}^{14}\text{O}^{14}$ ...	362	100.00	100.0	

Decomposed when boiled with dilute *nitric acid*, yielding binitro-hydrokinone,  $\text{C}^{12}\text{X}^2\text{H}^4\text{O}^4$ .

Easily soluble in *water*. The solution does not precipitate *metallic salts*. Slightly soluble in *alcohol*; insoluble in *ether*.

#### 2. Resin from *Arctostaphylos Uva Ursi*.

KAWALIER. *Wien. Akad. Ber.* 9, 297.

The mother-liquor remaining in the preparation of arbutin, according to page 420, yields, when mixed with hydrochloric or sulphuric acid, and warmed, a precipitate of a resin, which may be purified by solution in alcohol, and precipitation of the solution with water.



Brittle, black resin, easily reduced to a dark-brown powder, which melts when *heated*, and burns with a smoky flame.

	at 100°.		Kawaler.	
80 C .....	480	...	62.90	62.95
35 H .....	35	...	4.58	5.06
31 O .....	248	...	32.52	31.99
<hr/>				
C <sup>80</sup> H <sup>35</sup> O <sup>31</sup> .....	763	...	100.00	100.00

So, according to Kawaler. — Perhaps it is C<sup>24</sup>H<sup>11</sup>O<sup>9</sup>, and is produced from arbutin by loss of 5 at. water (calculation: 63.4 p. c. carb., 4.84 hydrog.). [Kr.]

### Amygdalin.



ROBIQUET & BOUTRON-CHARLARD. *Ann. Chim. Phys.* 44, 352; *Pogg.* 20, 494; *Schw.* 61, 223; *N. Tr.* 24, 2, 198. — *J. Pharm.* 23, 605; *Ann. Pharm.* 25, 175.

WÖHLER & LIEBIG. *Ann. Pharm.* 22, 1; *Pogg.* 41, 345.

Discovered by Robiquet & Boutron in 1830. The relation of amygdalin to its products of decomposition, and the part it plays in the production of oil of bitter almonds (xii, 20), were first explained by Wöhler & Liebig's investigation (1835). — Amygdalin was the first known example of a substance which yielded sugar as a product of decomposition.

*Occurrence.* In bitter almonds, the kernels of *Amygdalus communis*, var. *amara* (*Handb.* viii, *Phytochem.* 14. Robiquet & Boutron.). — The almonds contain amygdalin ready formed; it is not first produced on treating them with alcohol. If the concentrated aqueous emulsion is mixed, immediately after its preparation, with a very large quantity of absolute alcohol, the pulp pressed between linen, and the liquid filtered, boiled, filtered again, and evaporated, crystallised amygdalin remains behind (Wöhler & Liebig). In this manner, amygdalin may be obtained from the emulsion of dry but not of fresh almonds, which latter perhaps do not contain amygdalin ready formed (Winckler, *Repert.* 65, 15).

The following plants or part of plants either yield crystallised amygdalin, — or on subjecting them to the usual process for the preparation of amygdalin, an extract is obtained (Winckler's *amorphous amygdalin*), which, when treated with almond-milk, yields prussic acid and bitter-almond oil, but does not deposit any crystals of amygdalin. In other cases, the existence of amygdalin is indicated by the presence of prussic acid in the watery distillate, although no attempt may have been made to separate it: (See also vii, 389.)

*Amygdalus persica* (*Handb.* viii, *Phytochem.* 14). Peach-kernels contain about 3 per cent. of crystallised amygdalin (Geiseler, *Repert.* 68, 289); the leaves contain amorphous amygdalin. — *Prunus Laurocerasus*. The ripe kernels contain crystallised amygdalin (*Repert.* 65, 14); the leaves, amorphous amygdalin (Widtmann, *Repert.* 45, 429. — Denk, *Repert.* 45, 434. — Liebig & Wöhler, Winckler; Simon, *Ann. Pharm.* 31,

263. — Lepage, *J. Chim. méd.* 24, 365; abstr. *N. J. Pharm.* 15, 40). — *Prunus avium*. Cherry-stones contain amorphous amygdalin in quantity sufficient to yield as much prussic acid as corresponds to 2.1 p.c. crystallised amygdalin (Geiseler, *Repert.* 69, 289. — Winckler). — The green parts of the cherry-tree do not yield a distillate containing prussic acid (Wicke, *Ann. Pharm.* 79, 82). — *Prunus domestica*. Plum-stones contain crystallised amygdalin, together with a peculiar bitter substance (Winckler, *Repert.* 66, 327). The distillate from the very young shoots contains prussic acid; that from the older shoots contains none. (Wicke.) A distillate containing prussic acid is obtained from the leaves of *Prunus capricula*, the bark of *Pr. virginiana*, the flowers (Zeller), and the kernels of *Pr. spinosa* (Enz, *Pharm. Viertelj.* 6, 179), but not from the buds, leaves, root or bark of *Prunus Mahaleb* (Wicke, *Ann. Pharm.* 79, 82 and 81, 241). — *Prunus Padus*. From the fruit-kernels, Heumann (*Repert.* 75, 221 and 360) obtained  $1\frac{1}{2}$  per cent.; from the flowers, leaves and bark, Riegel (*Jahrb. pr. Pharm.* 4, 342) obtained from  $\frac{2}{3}$  to 1 p.c. of crystallised amygdalin; the plant also contains amorphous amygdalin (Riegel; Winckler, *Jahrb. pr. Pharm.* 4, 345; Heumann, Simon, Widmann, Denk). The distillate from the bark and leaves is richer in prussic acid in December than in the earlier part of the year (Wicke, *Ann. Pharm.* 81, 241).

The following *Pomeæ* (*Handb.* viii, *Phytochem.* 16). — *Crataegus oxyacantha*, *Cotoneaster vulgaris*, *Amelanchier vulgaris* (not *Pyrus Malus*), *Sorbus Aucuparia*, *S. hybrida* and *S. torminalis*—yield a distillate containing prussic acid. The amygdalin accumulates in the buds and bark of these plants during the autumn and diminishes during the period of growth. (Wicke, *Ann. Pharm.* 79, 79, and 81, 249). — The leaves of shrubby spiræas (*Handb.* viii, *Phytochem.* 15), *Spiræa Aruncus*, *S. sorbifolia* and *S. japonica* yield prussic acid, whereas the distillate of herbaceous spiræas contain either salicylous acid or neither of these acids (Wicke, *Ann. Pharm.* 83, 175; compare xiv, 235, and *Handb.* viii, *Phytochem.* 15).

*Preparation.* 1. The paste of bitter almonds freed from fixed oil by strong pressure is twice boiled with alcohol of 94 or 95 p. c., and the residue is strained and pressed. The oil which still separates on standing is removed, and the liquid after filtration is set aside, a small portion of the amygdalin then crystallising out. The remaining liquid is distilled till only a sixth portion of it remains; the residue is mixed with half its volume of ether which precipitates the amygdalin; the crystalline pulp is collected on a filter, pressed between bibulous paper renewed till it no longer takes up any fixed oil,—then shaken up, and the amygdalin washed with ether, till this liquid evaporated on the water-bath no longer leaves a film of oil; and finally recrystallised from boiling alcohol (Liebig & Wöhler).

Bitter almonds thus treated yield  $2\frac{1}{2}$  p. c. amygdalin. — Weaker spirit likewise extracts sugar and other substances from the almonds, decomposes the amygdalin, and renders the purification difficult; if no ether is used, part of the amygdalin remains in the mother-liquor after the alcohol is evaporated. It is not necessary to distil off more than half the alcohol, as ether will then precipitate nearly all the amygdalin from the residue after a few days. (Liebig & Wöhler, *Ann. Pharm.* 28, 329; Compare the similar process of Robiquet & Boutron; also that of Trommsdorff, *Ann. Pharm.* 27, 224).

2. The paste from 6 pounds of bitter almonds is boiled for an hour with 12 pts. alcohol, strained through sack-cloth and pressed, and the residue is boiled with 9 pounds of alcohol, and pressed again. The extracts when cold, are freed as much as possible from fixed oil by decantation and filtration, then from alcohol by distillation, and strained; the greater part of the fixed oil which still remains, is then left on the cloth in the form of a frothy mass. The crystalline pulp thus obtained in the course of 24 hours is triturated and washed with cold alcohol, pressed between linen, and crystallised from 2 pounds of boiling alcohol. By this process, large bitter almonds yield about 3 per cent., the smaller kind, 2·2 p. c. amygdalin. (Bette, *Ann. Pharm.* 31, 211.) Winckler (*Repert.* 65, 1), and Hänle (*Repert.* 67, 38, 3; *Jahrb. pr. Pharm.* 2, 163) proceed in a similar manner.—3. Bitter-almond paste is boiled with alcohol, the tinctures completely freed from alcohol by distillation, and the syrup, after dilution with water, is mixed with yeast. When the fermentation is ended, the liquid is evaporated to a syrup, and mixed with alcohol, which throws down nearly all the amygdalin as a white crystalline powder, which may be pressed and purified by recrystallisation. The syrup obtained by evaporating the fermented liquid might also be boiled with alcohol and filtered hot. (Liebig & Wöhler, *Ann. Pharm.* 24, 45).

The amygdalin remaining in the mother-liquors may be utilised by decomposing it with almond-milk, and distilling off the bitter-almond water. (Hänle.)

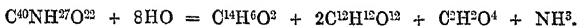
*Amorphous Amygdalin.* Chopped laurel-leaves are digested and boiled with alcohol, and the mass is strained, pressed, and freed from alcohol by distillation. The residue is freed from chlorophyll by ether, and from tannin by precipitating the solution with nitrate of lead; the lead is removed from the filtrate by sulphate of soda; the liquid is then evaporated, and the residue boiled with absolute alcohol. The extract when evaporated leaves an amorphous, yellow, tough resin, which when redissolved in absolute alcohol leaves a small quantity of sulphate of soda, and may be partially decolorised by animal charcoal. The dark yellow, transparent residue dissolves readily in water and alcohol, not in ether; it tastes like salicin and yields with almond-milk the same products as amygdalin (Winckler, *Repert.* 65, 1). Simon agitates the tincture of dried laurel-leaves with litharge, and evaporates the wine-yellow filtrate, which is free from lead. The light brown extract cannot be made to crystallise, but it exhibits with almond-milk and baryta-water, the same reactions as amygdalin. (*Ann. Pharm.* 31, 263.)

*Properties.* Crystallised amygdalin (see below) contains water, from which it may be freed by continued heating to 120° (Liebig & Wöhler). It melts at 200°, and solidifies to an amorphous mass, which, if again heated, melts between 125° and 130°. (Wöhler, *Ann. Pharm.* 41, 155). Inodorous, tastes sweet at first, afterwards bitter. (Robiquet & Boutron.) Neutral. Lævo-rotatory (see p. 428.). Does not act as a poison taken internally. Only in two instances, Wöhler & Frerichs saw dogs fall ill after taking large quantities of amygdalin; in these cases, they [as well as Widtmann (*Repert.* 45, 429) and Denk (*Repert.* 45, 434)], observed an odour of prussic acid in the breath, which odour was likewise emitted by the urine after addition of almond-milk. (Wöhler & Frerichs, *Ann. Pharm.* 65, 337; *Chem. Gaz.* 148, 229.)

at 120°.				Liebig & Wöhler.	Chiozza. mean.
40 C	240	...	52.51	51.54	52.20
N	14	...	3.06	3.06	
27 H	27	...	5.91	6.00	5.95
22 O	176	...	38.52	39.40	
$C^{40}NH^{27}O^{22}$				100.00	100.00

See also Liebig (*Ann. Pharm.* 18, 327); Henry & Plisson's analysis (*J. Pharm.* 16, 609). Mulder (*J. pr. Chem.* 15, 453), found 2.8 p. c. nitrogen; Varrentrapp & Will (*Ann. Pharm.* 39, 282) found 3.04 p. c.

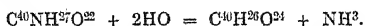
Amygdalin contains the elements of prussic acid, bitter-almond oil, and sugar (Wöhler & Liebig), or those of 1 at. cyanide of benzoyl ( $C^{14}H^5O^2, Cy$ ) and 2 at. gum (Wöhler, *Ann. Pharm.* 66, 238). It may be regarded as formed by the union of 5 groups of atoms, the conjugation of which is attended with the elimination of 8 at. water:



(Piria, *Ann. Pharm.* 96, 381). See also Gerhardt (*Précis* 1, 148; *N. Ann. Chim. Phys.* 7, 137).

*Decompositions.* 1. Amygdalin melts when heated, to a transparent liquid, which turns brown (at 160°, according to O. Schmidt), and gives off an odour of-caramel, then of white-thorn, together with an empyreumatic animal odour (Robiquet & Boutron, Widtmann).—2. It is not at all altered by ozone at the temperature of the air (Gorup-Besanez, *Ann. Pharm.* 110, 106).—3. Heated with *nitric acid*, it yields benzoic acid (Robiquet & Boutron) and bitter-almond oil (Peligot).—4. Aqueous amygdalin is not altered by heating with *mercuric oxide* or *peroxide of manganese*; but on addition of a small quantity of dilute sulphuric acid, carbonic acid escapes with violent action, while bitter-almond oil, benzoic acid and formic acid pass over, and an ammonia-salt remains in the residue (Wöhler & Liebig).—5. When aqueous amygdalin is gently heated with *permanganate of potash*, the solution becomes decolorised, depositing hydrated peroxide of manganese, while cyanate and benzoate of potash, produced by the reaction, remain dissolved: the former is decomposed at the boiling heat, in consequence of which, ammonia escapes and the residue becomes alkaline (Wöhler & Liebig).—6. When amygdalin is immersed in potash- or soda-ley, and *iodine* or *bromine* is added till the liquid becomes permanently coloured, a large quantity of bitter-almond oil is formed (Lifert, *Compt. rend.* 23, 229).—7. Dry *chlorine gas* does not act upon amygdalin; but in presence of water the mass swells up, and a white, inodorous, friable substance is formed, insoluble in water and in alcohol. (Robiquet & Boutron).—8. Amygdalin dissolves with light violet-red colour in *oil of vitriol* (Winckler). On boiling it with dilute sulphuric acid, small quantities of bitter-almond oil and formic acid are volatilised, and an additional quantity of the former after the residue has been neutralised with potash-ley. On neutralising with carbonate of baryta and evaporating, an amorphous baryta-salt is obtained, and the solution exhibits the power of reducing cupric salts (Chiozza, *Gerh. Traité*, 3, 200).—9. The solution of amygdalin in *fuming hydrochloric acid* acquires a yellow or brown colour when warmed, and at a higher temperature deposits black-brown humous substances, the filtrate when evaporated, leaving a mixture of humic acid, sal-ammoniac, and mandelic acid

(xii, 57), the last of which may be dissolved out by ether. If the liquid is evaporated at a temperature above  $100^{\circ}$ , part of the mandelic acid becomes amorphous (Wöhler, *Ann. Pharm.* 66, 239). Alcoholic hydrochloric acid appears to form amygdalate of ethyl (p. 430). By boiling with *dilute hydrochloric acid*, amygdalin is easily converted, without colouring, into bitter-almond oil, sugar, prussic acid and formic acid (Ludwig, *N. Br. Arch.* 82, 138; 87, 273).—10. By boiling with *potash-ley*, it is decomposed, with evolution of ammonia. (Robiquet & Boutron, Widtmann.) Amygdalic acid is formed as a second product (Wöhler & Liebig):



100 pts. amygdalin yield 103.57 pts. amygdalate of baryta (Wöhler & Liebig). Amygdalin, by conversion into amygdalic acid, acquires an increase of rotatory power. (Bouchardat, *Compt. rend.* 19, 1174). A similar result is produced by boiling with *baryta-water*; but when amygdalin is triturated with *anhydrous baryta* and gently warmed, a violent reaction takes place, by which ammonia is evolved, together with a white vapour which condenses to a colourless oil, and the brown residue contains carbonate of baryta. (Wöhler & Liebig.)

11. In contact with the *emulsin* of almonds (or with almond-milk) aqueous amygdalin is decomposed, with formation of bitter-almond oil, prussic acid and sugar (Wöhler & Liebig).



On the sugar thus produced see page 341.

When bitter almonds are freed from fixed oil by ether, the residue dissolves almost completely in water, to a faintly opalescent liquid from which alcohol throws down the *emulsin* in flocks. These flocks dissolve in water even after drying, and the solution becomes turbid between  $60^{\circ}$  and  $70^{\circ}$ , and solidifies at  $100^{\circ}$  to a stiff paste no longer soluble in water. Emulsin which has been dried is still capable of decomposing amygdalin, but that which has been coagulated by heat no longer possesses this power. When bitter almonds are completely freed from amygdalin by exhaustion with cold alcohol, the residue, mixed with water, still acts on amygdalin (Wöhler & Liebig), but the residue left after exhausting the residue obtained by exhausting the almonds with hot alcohol still yields, when treated with water, a soluble emulsin, which is coagulated by heat, and precipitated by tannic acid, but no longer acts on amygdalin (Robiquet & Boutron).

The aqueous solution of almonds exhausted with ether becomes somewhat more opalescent on addition of amygdalin, but does not deposit any bitter-almond oil on cooling, whatever may be the quantity of amygdalin or emulsin contained in it, because the decomposition of the amygdalin goes on only so long as sufficient water is present to dissolve all the products of decomposition. The mixture coagulates when distilled and gives off considerable quantities of bitter-almond oil, more if the action has been continued for 6 or 8 hours, than if the mixture is heated immediately. 1 pt. of emulsin is capable of decomposing about 10 times its weight of amygdalin in 8 days, provided a sufficient quantity of water is present (Wöhler & Liebig:—Liebig, *Chemische Briefe*, 172). When sweet almonds are triturated with a small quantity of water and a quantity

of sugar too large to dissolve completely, the odour of bitter-almond oil is not evolved on adding pulverised amygdalin, but powerfully on subsequent addition of cold water.

Besides bitter-almond oil, sugar, and prussic acid, other products are formed, probably by decomposition of those first produced. Wöhler & Liebig gave the equation,



but they found more sugar than it requires (*Handwörterbuch*, 2 Aufl. 1, 766): the formula of decomposition given above (p. 426) is therefore to be preferred. If the sugar thus formed be decomposed by fermentation, the residue becomes acid in consequence of the presence of a non-volatile acid (succinic acid? Kr. see page 275). If the solution is somewhat concentrated, alcohol throws down thick white flocks of gum, perhaps produced by alteration of emulsin (Wöhler & Liebig). When amygdalin is gently warmed with emulsin and water, ammonia is given off. On agitating the mixture with oxide of silver, the previously acid liquid becomes alkaline, and gives off ammonia when placed in a vacuum. Since cyanide of silver is also produced, 2 at. of amygdalin must be engaged in the reaction. (Deschamps, *J. Pharm.* 25, 22; *N. Ann. Chim. Phys.* 12, 383.)

The action of the emulsin is prevented by the addition of 1 pt. hydrate of soda or oil of vitriol to 100 pts. of the amygdalin, and retarded by an equal addition of lime, magnesia, ammonia, or carbonate of ammonia, hydrochloric acid or oxalic acid; whereas bicarbonate of soda, most other acids and salts, alkaloids and volatile oils (especially oil of mustard, arsenic acid, prussic acid, sulphate of copper, and cyanide of silver) do not exert any retarding action. (Bouchardat, *Compt. rend.* 20, 110.)

It is only the emulsin of almonds that is capable of decomposing amygdalin, not the albumin of other plants. (Wöhler & Liebig, Robiquet & Boutron.) If 1 pt. of the seed of bitter or sweet almonds, poppy, hemp, black mustard, or white mustard, be triturated to a milk with 8 pts. water, the liquid precipitated with alcohol, and the precipitate washed with ether and alcohol, emulsin is obtained, capable of decomposing amygdalin, but in various degrees, and in different times. The strongest action is produced by the emulsin of bitter almonds. (E. Simon, *Pogg.* 43, 404.) Active emulsin may also be obtained from the leaves of the cherry-laurel and the bark of *Prunus Padus*. (Simon, *Ann. Pharm.* 31, 263.)

A mixture of sweet-almond milk and amygdalin is recommended by Wöhler & Liebig, instead of bitter-almond water, as a pharmaceutical preparation containing a definite proportion of prussic acid. (*Ann. Pharm.* 22, 24, and 23, 329.) Such a mixture is less likely to spoil than almond-milk alone. (Hänicke, *Repert.* 67, 387.)

11. Amygdalin is decomposed by a certain substance in the yolk of egg, in the same manner as by emulsin (Barreswil, *N. J. Pharm.* 17, 118). *Diastase*, which has not been heated, forms bitter-almond oil from amygdalin in a few days; a mixture of yeast, sugar-water and amygdalin, kept for some months, emits a strong odour of prussic acid. (Robiquet & Boutron.) Amygdalin is not decomposed by yeast (Schlossberger, *Ann. Pharm.* 51, 211), but in contact with yeast, bicarbonate of soda, and a large quantity of water at 17°, it emits the

odour of bitter-almond oil, and is completely decomposed, with formation of formic acid, ammonia, and crystals soluble in alcohol and ether. (Ranke, *J. pr. Chem.* 56, 16.)

Amygdalin is not decomposed by *calf's rennet* (Wöhler & Liebig), by the secretion of the pancreas (O. Schmidt, *Ann. Pharm.* 92, 35), or by *saliva* (provided it does not act as a poison). — Ranke (*J. pr. Chem.* 56, 16) after injecting 5 grammes of amygdalin, together with milk, into the stomach of a rabbit, found that the acid urine contained formic acid.

*Combinations.* With *Water*. — Amygdalin, when dry, greedily absorbs from 2 to  $3\frac{1}{2}$  p. c. water. (Wöhler & Liebig.)

A. *Quadro-hydrated Amygdalin*. — Amygdalin crystallised by drying over oil of vitriol, or by separation from alcohol of 80 p. c., contains 4 at. water. Colourless nacreous scales. (Wöhler & Liebig.)

B. *Sex-hydrated (crystallised) Amygdalin*. — Separates from the aqueous solution in transparent prisms, which, when left over oil of vitriol, give off 3.52 p. c. water (2 at. H<sub>2</sub>O = 3.52 p. c.), and become less transparent; at 120°, they give off 10.57 p. c. water (6 at. = 10.56 p. c.), being thereby converted into anhydrous amygdalin. (Wöhler & Liebig.) Colourless right prismatic crystals having the character of *Figure 55*.  $u : u = 127^\circ 0'$ ;  $u : l = 113^\circ 39'$ ;  $i : l = 96^\circ 13'$ . A second horizontal prism (corresponding to  $u$  of figure 53), as well two octahedrons could not be measured on account of the strong curvature of their faces. Cleavage very perfect parallel to  $i$ , but imperfect in the direction perpendicular thereto (parallel to  $l$ , *Fig. 53*). Lustre vitreous, pearly on  $i$ . The crystals, which are 10 mms. long, are united into bundles by the faces  $i$  (Keferstein, *Pogg.* 99, 293). — *Lævo-rotatory*: for amygdalin (? quadro-hydrated), dried at 45° over lime,  $[\alpha]_D = -35.51^\circ$ . (Bouchardat, *Compt. rend.* 19, 1174.)

	Over oil of Vitriol.		O. Schmidt.	
40 C .....	240	...	46.96	..... 46.69
N .....	14	...	2.74	..... 2.57
33 H .....	33	...	6.46	..... 6.65
28 O .....	224	...	43.84	..... 44.09
<hr/>				
C <sup>40</sup> NH <sup>27</sup> O <sup>22</sup> + 6aq. ....	511	...	100.00	..... 100.00

Amygdalin is easily soluble in water. The solution does not precipitate any *metallic salt*.

It is nearly insoluble in cold *alcohol*, but dissolves very easily in boiling alcohol; the solution in alcohol of 94 to 95 p. c. still retains  $\frac{1}{16}$  in solution after cooling.

Amygdalin crystallised from absolute alcohol appears to hold alcohol in combination, which is not easily removed by heating. (Wöhler & Liebig.) — Anhydrous and quadro-hydrated amygdalin dissolve but sparingly even in hot alcohol; but the solution obtained by dissolving sex-hydrated amygdalin in absolute alcohol may be evaporated to a syrup without yielding crystals, which, in fact, do not form till it has been left for some days in a warm place. (Winckler, *Repert.* 65, 5.)

Amygdalin is insoluble in *ether*.

# Amygdalic Acid.



WÖHLER & LIEBIG. *Ann. Pharm.* 22, 11.

*Formation*, p. 426.

Amygdalin is dissolved in baryta-water, the solution is boiled for a quarter of an hour, or as long as it continues to evolve ammonia; carbonic acid is then passed through the hot liquid, and the carbonate of baryta is separated by filtration. From the resulting aqueous solution of amygdalate of baryta, *aqueous amygdalic acid* is obtained, by carefully precipitating with dilute sulphuric acid, and removing the sulphate of baryta, as a slightly acid liquid, which dries up to a gum when evaporated over the water-bath. The concentrated aqueous solution left for some time in a warm place, yields traces of crystals (Wöhler & Liebig).—Laevo-rotatory; for the acid dried at 60° for several days  $[\alpha]_D = -40.19^\circ$ . (Bouchardat, *Compt. rend.* 19, 1174.)

It is not altered by boiling with *peroxide of manganese*; but on subsequent addition of dilute sulphuric acid, it gives off carbonic acid, formic acid, and bitter-almond oil. — When amygdalate of baryta is precipitated with *sulphate of silver*, sulphate of baryta is precipitated having a brown colour; which becomes darker on heating, from separation of metallic silver. At the same time an odour like that of formic acid, becomes apparent.

Amygdalic acid deliquesces in moist air, and dissolves to a syrup in a small quantity of *water*.

The amygdalates are gummy and uncrystallisable. (Wöhler & Liebig.) The rotatory power of the acid is not altered by neutralisation with baryta or ammonia. (Bouchardat.)

*Amygdalate of Baryta*. — *Preparation* see above. — Remains, when its aqueous solution is evaporated, in the form of a gum, which gives off water at 140°, becomes white and like porcelain at a higher temperature, which may be raised as high as 190°, and is then easily rubbed to a fine powder, which greedily absorbs from 4 to 7 p. c. water, on exposure to the air.

	at 190°.		Wöhler & Liebig.
			mean.
40 C .....	240.0 ....	44.91 .....	44.35
26 H .....	26.0 ....	4.86 .....	5.03
24 O .....	192.0 ....	35.92 .....	36.44
BaO .....	76.5 ....	14.31 .....	14.18
<hr/>			
$\text{C}^{40}\text{H}^{26}\text{O}^{24}, \text{BaO}$ ....	534.5 ....	100.00 .....	100.00

So, according to Wöhler & Liebig; Gerhardt (*Traité* 3, 201) writes the formula  $\text{C}^{40}\text{H}^{26}\text{BaO}^{24}, \text{HO}$ .

*Amygdalate of Lime*. — Obtained by neutralising the acid with milk of lime, and filtering through charcoal (to remove the excess of lime ?). Laevo-rotatory;  $[\alpha]_D = -41.24^\circ$  (Bouchardat, *Compt. rend.* 19, 1174).



*Amygdalate of Zinc.*—By double decomposition of the lime-salt with sulphate of zinc, and removal of the sulphate of lime with alcohol. Gummy mass, having a molecular rotatory power,  $[\alpha]_D = -40.48^\circ$  (Bouchardat).

*Amygdalate of Lead.*—From aqueous amygdalates, ammoniacal sugar of lead throws down a white precipitate, which gradually dissolves during washing. (Wöhler & Liebig.)

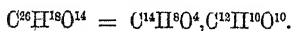
Amygdalic acid dissolves sparingly in aqueous alcohol, but is insoluble in absolute alcohol, whether cold or boiling, also in ether. (Wöhler & Liebig.)

### Amygdalate of Ethyl.

WÖHLER. *Ann. Pharm.* 66, 240; *J. pr. Chem.* 44, 382; *Pharm. Centr.* 1848, 840.

*Amygdalic ether, Amygdalinsäurevinester.* When hydrochloric acid gas is passed into a pasty mixture of amygdalin and alcohol, the amygdalin dissolves, and does not separate on cooling. The faintly brown liquid, after a few days, deposits sal-ammoniac, a further quantity of which is precipitated on addition of ether. On mixing the liquid with a considerable quantity of ether, an acid aqueous solution of sal-ammoniac falls to the bottom, and above it there floats an ethereal liquid which leaves a light-brown syrup when evaporated. This syrup is heavier than water, and not miscible therewith, but dissolves with decomposition in warm water.

### Salicin.



LEROUX. *J. Chim. méd.* 6, 341; *Schw.* 59, 356; *Ann. Chim. Phys.* 43, 440.

BRACONNOT. *Ann. Chim. Phys.* 44, 296; *Pogg.* 20, 47; *N. Tr.* 23, 2, 261; *Br. Arch.* 36, 226; *Repert.* 36, 280. — *J. Chim. méd.* 7, 17; *Pogg.* 20, 621.

PELOUZE & GAY-LUSSAC. *Ann. Chim. Phys.* 44, 220; *Ann. Pharm.* 1, 43; *Ann. Chim. Phys.* 48, 111.

PIRIA. 1. *Compt. rend.* 6, 388; *J. pr. Chem.* 13, 500. — 2. *Compt. rend.* 6, 620; *J. pr. Chem.* 14, 285. — 3. *Compt. rend.* 7, 935; *J. pr. Chem.* 16, 412; *Ann. Pharm.* 29, 300. 1 to 3, in detail: *Ann. Pharm.* 30, 151; *J. pr. Chem.* 17, 241; *Ann. Chim. Phys.* 69, 281. — 4. *Compt. rend.* 17, 168; *J. pr. Chem.* 30, 249; in detail: *Ann. Pharm.* 56, 49; *J. pr. Chem.* 36, 321; *N. Ann. Chim. Phys.* 14, 257 and 272. — 5. *Ann. Pharm.* 96, 375; *N. Ann. Chim. Phys.* 44, 336.

BOUCHARDAT. *Compt. rend.* 181, 299; *J. pr. Chem.* 32, 89. — *Compt. rend.* 19, 602; 20, 110; 20, 1635.

GERHARDT. *N. Ann. Chim. Phys.* 7, 215; *Ann. Pharm.* 45, 19.

Discovered by Leroux in 1830, after a previous attempt by Buchner (*Repert.* 29, 417; 34, 107) to isolate the bitter principle of willow bark. Keller (*Repert.* 39, 268) and Peschier (*J. Chim. méd.* 6, 651; *Schw.* 61, 208) ascribed basic properties to salicin; Buchner & Herberger (*Repert.* 37, 58) regarded it as a salt; their errors were pointed out by Duflos, Hopff, Braconnot, and others. — Chiefly investigated by Pinia.

*Occurrence.* In many species of willow, but not in all; most abundantly (to the amount of 3 to 4 p.c.) in the bark of *Salix Helix*, *S. pentandra* and *S. præcox*, but likewise in the leaves, female flowers and young twigs. The bark of young willow and poplar branches contains more salicin than that of the older branches, and a smaller proportion of substances which impede its purification; the leaves contain a smaller quantity, and when they turn red in the autumn, none at all (Herberger). The strong bitter taste of willow bark is due to salicin; sweet tasting willow barks, like that of *Salix phylicifolia* (and, according to Duflos, those which are not reddened by oil of vitriol) contain none. — In *Salix alba* (Peschier, Leroux), not according to Braconnot; in *S. amygdalina* (Herberger; Leroy, *J. Chim. méd.* 14, 87; Braconnot), not according to Duflos; not in *S. argentea* (Duflos); not in *S. babylonica* (Herberger), *S. bicolor*, *S. caprea*, *S. daphnoides*, but in *S. fissa* (Braconnot); in *S. confusa* and *S. fragilis* (Herberger, Lasch); not in the latter, according to Braconnot; in *S. hastata* (Peschier, Lasch), *S. Helix* (Leroux, Braconnot; Gruber, *Oesterr. med. Jahrb.* 11, 316; Fr. Esenbeck & Becker, *Ann. Pharm.* 4, 33); *S. incana* (Peschier, Buchner), not according to Braconnot; *S. lambertiana* (Lasch); *S. mollissima* and *S. nigra* (Herberger); *S. pentandra* (Herberger, Lasch; Erdmann, *Berl. Jahrb.* 33, 1, 136); *S. præcox* (Peschier, Herberger, Lasch); *S. purpurea* (Lasch, Herberger; Pleisch, *Zeitschr. Phys. Math.* 3, 322); in *S. reticulata*, *S. retusa* and *S. rubra* (Herberger); in *S. Russelliana* according to Duflos, not according to Braconnot; not in *S. triandra* (Braconnot); in *S. viminalis*, according to Herberger & Hopff; not, according to Braconnot; in *S. vitellina* according to Buchner, Herberger & Lasch (*N. Br. Arch.* 2, 78), not, according to Duflos and Braconnot. — In the bark and leaves of various species of poplar. In *Populus alba* (Braconnot; Tischhauser, *Berl. Jahrb.* 34, 2, 126; Herberger); not in *P. angulosus* or *P. balsamifera* (Braconnot); it exists in the latter, according to Herberger and Wittstein (*Pharm. Viertelfahr.* 6, 47); in *P. canescens* (Herberger), *P. græca* and *P. tremula* (Herberger, Braconnot); in *P. dilatata*, *P. nigra*, *P. tremuloides* (Herberger, *Jahrb. pr. Pharm.* 1, 157); not, according to Braconnot; also not in *P. fastigiata*, *P. grandiculata*, *P. monilifera* or *P. virginica* (Braconnot). — The herbaceous spiræas mentioned at page 235, vol. xii, contain salicin, inasmuch as when distilled with water they yield salicylous acid (Wicke, *Ann. Pharm.* 83, 175). The flower-buds of *Spiræa ulmaria* yield a small quantity of salicylous acid when distilled with water, more after the addition of bichromate of potash, the acid being doubtless formed by decomposition of salicin (Buchner, *N. Repert.* 2, 1; *Ann. Pharm.* 88, 284). — *Castoreum canadense* contains salicin (Wöhler, *Ann. Pharm.* 67, 360).

*Formation.* By boiling populin with baryta- or lime-water, or, together with benzoic acid, by heating populin with alcoholic ammonia. If the benzoic acid be precipitated by ferric chloride, the excess of iron removed by milk of lime, and the lime with carbonic acid, the

concentrated filtrate yields crystals of salicin (Piria, *Ann. Pharm.* 96, 375).

*Preparation.* From *willow* or *poplar bark*; according to Herberger, it cannot be obtained pure from poplar bark, and is therefore better prepared from willow bark, although the latter contains less of it. When poplar bark is used, populin may crystallise out, either before or together with the salicin (see below).

1. Six pounds of the dry chopped bark are boiled with water; the liquid is strained, concentrated down to 18 pounds, mixed while still hot with 2 pounds of levigated oxide of lead, and digested for 24 hours. The liquid is strained, the residue thoroughly washed, and the filtrate evaporated to a syrup and left to crystallise. An additional quantity of salicin is obtained from the mother-liquors after they have again been treated with oxide of lead, and the entire product is purified by repeated crystallisation (Duflos, *Schw.* 67, 25). — 2. The aqueous decoction of the bark is precipitated with basic acetate of lead; the filtrate is boiled with chalk, till the excess of the basic acetate is decomposed, and the liquid becomes clear and colourless; it is then evaporated to an extract; this is exhausted with alcohol of 34°, and the solution is left to crystallise (Peschier, *Ann. Chim. Phys.* 44, 418). — 3. Sixteen parts of bark are macerated with 2 pts. lime and with water for 24 hours; the mixture is boiled for half an hour, and strained; the residue is treated in like manner with the same quantity of lime as before; and the whole of the liquids are decanted from the sediment, concentrated, then mixed with 6 to 8 pts. of bone-black, and evaporated to complete dryness. The residue, after being pulverised, is exhausted at a gentle heat with alcohol of 82 per cent., and the alcohol is distilled off from the tinctures: the salicin then crystallises from the residue in pale yellow granules, which are purified by recrystallisation, with help of animal charcoal (Erdmann, *Berl. Jahrb.* 33, 1, 136). — 4. A layer of recently ignited charcoal powder is placed at the bottom of a Rea's press; above it, a moist mixture of coarsely pulverised willow-bark and slaked lime, and the bark is exhausted with alcohol of 80 per cent., which is finally displaced by pouring water upon the mass. The pale yellow liquid, freed from alcohol by distillation, yields, on evaporation, crystals which are obtained pure by washing with cold water (Fr. Nees v. Esenbeck, *Br. Arch.* 35, 223).

Less simple modes of preparation are described by Leroux (*Schw.* 59, 356), Herberger (*Repert.* 55, 215), Hopff (*Br. Arch.* 37, 217), Tischhauser (*Ann. Pharm.* 7, 280), Tyson & Fischer (*J. Pharm.* 18, 170). See above.

*Properties.* Rectangular laminae with well developed terminal summits (Biot & Pasteur). Tabular or broad prismatic crystals of the rhombic or right prismatic system, mostly appearing in the form of white shining scales, needles or laminae. *Fig.* 68 without the *p*- and *y*-faces,  $t:u = 110^\circ 24'$ ;  $u:u = 139^\circ 12'$ ;  $u:u$  over  $t = 40^\circ 48'$ ;  $t:i = 111^\circ 51'$ ;  $i:i = 136^\circ 18'$ . Cleavage at right angles to the prismatic faces *u*, probably also parallel to the face *t*, which has a strong pearly lustre; the other faces have a pearly, vitreous lustre (Schabus, *Bestimmung.* 86). — Pleischl (*Zeitschr. Phys. Math.* 3, 322) describes crystals of the right prismatic system  $\frac{1}{4}$  inch long, and a line in thickness.

(Fig. 61),  $u:u = 109^\circ 55'$  and  $70^\circ 5'$ . Cleavage parallel to  $p$  and  $u$ . This cleavage and the angles of the prism do not accord with the determinations of Schabus.

From the solution of salicin in warm water acidulated with sulphuric acid, thick, short, transparent, four-sided prisms are obtained which grate between the teeth, and are as bitter as before this treatment (Braconnot). They have the same composition as ordinary salicin, and exhibit similar chemical reactions, but cannot be obtained from every kind of salicin.

Salicin melts at  $100^\circ$  without loss of weight, and solidifies in the crystalline form on cooling (Piria). Melts at  $198^\circ$  (O. Schmidt, *Dessert. Gött.* 1861, 19). Has a very bitter taste, like that of the willow. Inodorous, permanent in the air, neutral (Leroux, Gay-Lussac & Pelouze). Not poisonous; produces unpleasant symptoms only when taken in doses of an ounce daily (Ranke). Sp. gr. 1.426 to 1.434 at  $16^\circ$  (Piria). Lævo-rotatory,  $[\alpha]_D^{20} = -71.7^\circ$  to  $73.4^\circ$  (Bouchardat *Compt. rend.* 18, 298).

				J. Gay-Lussac & Pelouze.		Otto & Erdmann.		Marchand. mean.		Piria. mean.
26 C	.....	156	....	54.54	....	54.02	.....	54.51	.....	54.43
18 H	.....	18	....	6.29	....	6.38	.....	6.39	.....	6.38
14 O	.....	112	....	39.17	....	39.60	.....	39.10	.....	39.19
$C^{26}H^{18}O^{14}$	....	286	....	100.00	....	100.00	.....	100.00	....	100.00

Piria's salicin, which was obtained from populin, agreed in specific gravity, solubility (Piria), and molecular-rotatory power (Biot & Pasteur, *Compt. rend.* 34, 607) with willow salicin. — Earlier formulæ (and analyses) of salicin,  $C^8H^5O^4$  (J. Gay-Lussac & Pelouze, *Ann. Pharm.* 1, 43; *Ann. Chim. Phys.* 48, 111);  $C^{42}H^{28}O^{22}$  (Piria; Erdmann & Marchand, *J. pr. Chem.* 15, 302; Otto, *Ann. Pharm.* 29, 294; Otto & Erdmann, *J. pr. Chem.* 17, 305; Marchand, *J. pr. Chem.* 17, 306; Mulder, *J. pr. Chem.* 17, 299);  $C^{42}H^{28}O^{22}$  (Liebig, *Ann. Pharm.* 30, 185);  $C^{28}H^{19}O^{15}$  (Marchand, *J. pr. Chem.* 26, 392). Piria established the true formula by examination of the products of decomposition. See also Berzelius (*Jahresber.* 23, 496; 24, 525), Gerhardt (*N. Ann. Chim. Phys.* 7, 215), Marchand (*J. pr. Chem.* 30, 251).

*Decompositions.* 1. Salicin kept for some time in the melted state, acquires a brown colour, and a resinous friable consistence (J. Gay-Lussac & Pelouze). At a stronger heat it swells up, chars with smoke (Hopff), and yields by dry distillation an acid watery liquid, and a large quantity of brown oil, soluble in potash-ley, but free from benzoic acid (Braconnot). When salicin is heated to  $260^\circ$ , water and salicylous acid are given off, together with acid vapours having an odour of caramel, and there remains a yellow residue insoluble in water, which turns brown and ultimately chars (Gerhardt). By dry distillation a heavy yellow oil is obtained which boils above  $250^\circ$ , contains more carbon than salicylous acid ( $72.60$  C. and  $6.84$  H.), and when treated with potash-ley, yields salicylous acid (Marchand)). — 2. By the current of a Bunsen's battery of 400 pairs salicin is resolved into glucose and saligenin which latter is then converted into salicylous and ultimately into salicylic acid. A brown substance is formed at the same time (Tichanowitsch, *Petersb. Acad. Bull.* 4, 80; *abstr. Chem. Centr.* 1861, 613). — 3. Salicin is not altered by ozone. (Gorup-Besanez, *Ann. Pharm.* 110, 106.)

4. Peroxide of lead boiled with aqueous salicin gradually turns brown and dissolves in the form of formate of lead and a compound of salicin with lead-oxide. Sulphuric acid added to the filtrate throws down a

mixture of sulphate of lead and rutilin (Stenhouse *Phil. Mag. J.* 19, 39; *J. pr. Chem.* 26, 138). — When salicin is heated with *peroxide of lead*, *peroxide of manganese*, or *bichromate of potash*, and *sulphuric acid*, formic and carbonic acids are produced, in the last case also salicylous acid (Piria). When more than 3 pts. oil of vitriol are used to 4 pts. of bichromate of potash, saliretin is obtained instead of salicylous acid (Piria). — Döbereiner (*Ann. Pharm.* 3, 146) obtained a large quantity of formic acid from salicin by the action of manganese and sulphuric acid. See also xii, 236. — Salicin reduces permanganate of potash (Duflos, *Schw.* 61, 214).

5. In *chlorine-gas* salicin changes to a red, resinous, turpentine-like mass, while a large quantity of hydrochloric acid is given off. — When chlorine-gas is passed into a mixture of salicin and water, chloro- and bichloro-salicin are successively produced (Piria). Formerly Piria likewise obtained a product which he subsequently regarded as a mixture of bi- and per-chlorosalicin. — If the mixture be heated to 60° during the passage of the chlorine, a red oil is separated, probably bichlorosaliretin, resulting from the decomposition of bichlorosalicin by hydrochloric acid (Piria). Bromine and iodine likewise act upon salicin, with evolution of heat, and form resinous bodies similar to those which they produce from phlorizin (De Koninck). — When salicin is distilled with *chloride of lime* and water, chloropicrin (xi. 216) is obtained, but no chloranil (Stenhouse, *Ann. Pharm.* 55, 4; 66, 247). Aqueous chloride of lime does not form a yellow precipitate with salicin. — When soda-ley is poured upon salicin, and *iodine* or *bromine* added till coloration is produced, and the liquid evaporated in vacuo, salicylous acid is produced, but no salicylic acid. (Lefort, *Compt. rend.* 23, 229.)

6. Salicin immersed in cold *oil of vitriol* forms a fine purple-red solution, from which water throws down a dark-red powder, Braconnot's rutilin (Braconnot). The solution formed at 10° is decolorised by water; that produced at 30° is not; both solutions contain olivin, rutilin, and rufisulphuric acid (Mulder). With oil of vitriol, salicin yields rutilin and glucose (or products of its decomposition). (Piria.) Aqueous salicin is also reddened by oil of vitriol (Duflos, *Schw.* 67, 25).

When salicin is added to oil of vitriol, there is formed, as it dissolves, a bright red liquid, which loses its colour and deposits a red powder, if the oil of vitriol is allowed to absorb water from the air, but remains coloured if the oil of vitriol is diluted by addition of water, — also after neutralisation with alkalis. If the solution be diluted with its own weight of water and neutralised with pulverised carbonate of potash, sulphate of potash is precipitated mixed with rutilin; the latter when isolated by washing with water, has a yellowish liver-red colour, is tasteless, and insoluble in water, alcohol, and glacial acetic acid, even at the boiling heat. It is turned violet-red by alkalis, without dissolving, brighter red by acids, and dries up to a black-brown powder which yields picric acid with nitric acid, and leaves a large quantity of charcoal when heated. This formation of rutilin (likewise produced from populin) is attended with complete decomposition of the salicin. (Braconnot, *J. Chim. méd.* 17, 17; *Pogg.* 20, 621.)

a. *Mulder's Olivin*. — When 2 or 3 grammes of salicin are immersed in oil of vitriol at 15°, and the product is washed with water and dried at 130°, an olive-green crystalline product is obtained, containing on the average 68·67 p. c. C., 4·81 H., and 26·52 O., and answering, accord-

ing to Mulder, to the formula  $C^{14}H^6O^4$ . No other product appears to be formed (therefore perhaps salicin minus 7 at. water =  $C^{26}H^{11}O^7$ .—Kr.).—This olivin, when heated, gives off the odour of salicylous acid, and afterwards empyreumatic products. It is insoluble in boiling hydrochloric and dilute sulphuric acids, but dissolves, with violet colour, in warm oil of vitriol. When heated with nitric acid, it is first dissolved with red colour, and then decomposed. Insoluble in water, boiling potash-ley, alcohol, and ether. (Mulder.)

*b. Mulder's Rutilin (containing Sulphuric Acid).*—When larger quantities of salicin are introduced into oil of vitriol, part of it cakes together to a brown mass, enclosing still unaltered salicin. If this mass be freed by decantation from the greater part of the oil of vitriol, then shaken up with absolute alcohol, pulverised, and washed with water and alcohol, rutilin remains behind; it might also be separated by agitating with absolute ether the mass which remains after decanting the oil of vitriol, removing the upper milk-white layer of liquid, and precipitating the lower violet-blue liquid with absolute alcohol. This rutilin, according to the temperature at which it has been prepared, appears, either as a violet translucent jelly, which dries up to a violet powder or (at a higher temperature, between  $30^\circ$  and  $70^\circ$ ) as a hard brown powder. It dissolves with red colour in oil of vitriol, also in nitric acid, and is decomposed when heated therewith. After drying, it is insoluble in boiling potash-ley, but is taken up by it in presence of excess of sulphuric acid, and then separates on evaporation. It is insoluble in water, alcohol and ether. The products formed at  $40^\circ$ ,  $55^\circ$ , and  $70^\circ$  respectively, and dried at  $130^\circ$ , differ from one another in composition. (Mulder.)

	at $40^\circ$ .		at $55^\circ$ .		at $70^\circ$ .
C .....	65.28	.....	59.42	.....	64.48
H .....	4.65	.....	4.05	.....	4.59
O .....	14.33	.....	14.73	.....	19.63
SO <sup>3</sup> .....	15.74	.....	21.80	.....	11.30

100.00	.....	100.00	.....	100.00
--------	-------	--------	-------	--------

Mulder regards these substances as compounds of a radical  $C^{14}H^6$ , with variable quantities of oxygen and sulphuric acid. See his formulæ (*J. pr. Chem.* 18, 364).

*c. Mulder's Rufisulphuric acid.*—Contained in the red sulphuric acid solutions, produced by the action of oil of vitriol on salicin, and obtained in the form of a lime-salt, by diluting the sulphuric acid solution with water, neutralising with chalk, and evaporating the red filtrate. If the solutions, when evaporated, deposit rutilin in brown flocks, and becomes acid at the same time, the flocks of rutilin must be removed, the liquid again neutralised with chalk, evaporated, and so on as long as the solution continues to turn acid. The unaltered salicin may be removed from the residue by alcohol. The lime-salt (*a*) forms a chesnut-brown powder, which dissolves in a small quantity of water, but is insoluble in alcohol. In oil of vitriol it dissolves with red colour, which disappears on addition of water; in dilute acids without coloration. Another lime-salt (*b*) is obtained in the form of a jelly, by neutralising the sulphuric acid solution with chalk, and precipitating with alcohol. On dissolving this jelly in water and evaporating, sulphate of lime separates out, while the salt *a* remains in solution. At  $130^\circ$ , the lime-salt *a* contains 22.48 p. c. SO<sup>3</sup>, 8.06 CaO, 4.18 H., and about 40 C.; and *b* contains 32.37 p. c. SO<sup>3</sup>, 10.44 CaO, 3.30 H., and

33.3 C. Mulder estimates the carbon at a higher amount, supposing that carbonate of lime remained behind in the combustion. He regards the salts as compounds of sulphuric acid, water and lime, with a body  $C^{14}H^{10}O^8$ , said also to be produced under similar circumstances from phlorizin. (Mulder, *J. pr. Chem.* 18, 356.)

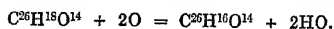
Salicin boiled with *dilute sulphuric* (or *hydrochloric*) *acid* is resolved into saliretin (xii, 231) and glucose. If the liquid be heated only till it begins to show turbidity (at 80°), and then cooled, the solution will be found to contain saligenin, which is therefore produced before the saliretin, but is converted into the latter before all the salicin is decomposed. (Piria.)

Formation of saligenin:  $C^{26}H^{18}O^{14} + 2H_2O = C^{14}H^{10}O^4 + C^{12}H^{12}O^{12}$ . — The transformation takes place even when the air is excluded. (Piria.) The complete decomposition is difficult, so that variable quantities of glucose are produced (Roser, *Ann. Pharm.* 74, 184)  $\frac{1}{100}$  pt. of hydrochloric acid mixed with aqueous salicin does not alter its rotatory power at 10° in 48 hours (Bourchadat, *Compt. rend.* 18, 298). When the solution in dilute hydrochloric acid, which is easily formed, is evaporated on a glass plate, unaltered salicin remains, but hot hydrochloric acid acts in the same manner as boiling dilute sulphuric acid. (Braconnot). — When hydrochloric acid gas is passed into alcoholic salicin, a splendid purple-red liquid is formed, from which water precipitates saliretin. (Roser.)

7. When small quantities of *hydrochloric acid* are added to a solution of salicin and chlorate of potash in boiling water, the mixture acquires a deep orange-yellow colour, gives off, with brisk effervescence, the products of the decomposition of chloric acid, together with a large quantity of carbonic acid, and becomes covered with crystals of chloranil, see xi, 196 (A. W. Hofmann, *Ann. Pharm.* 52, 64). A peculiar oil is formed at the same time. (Städeler, *Ann. Pharm.* 69, 327). Aqueous *iodic acid* at 110° oxidises only  $\frac{2}{3}$  of the carbon of salicin, unless it is employed in large excess (Millon, *Compt. rend.* 19, 271; *N. Ann. Chim. Phys.* 13, 37.)

8. Cold concentrated *nitric acid* dissolves salicin more abundantly than water, but does not decompose it; in fact on saturating the liquid (immediately? Kr.), the salicin is recovered with all its properties. (Braconnot). — By the prolonged action of nitric acid on salicin, there are produced, according to the temperature and strength of the acid, helicoidin, helicin, anilotic or nitrosalicylic acid, and lastly, if the salicin is heated with excess of nitric acid, the products are picric acid and oxalic acid.

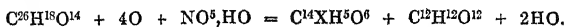
a. When nitric acid of 20° Bm. is poured upon salicin at the temperature of the air, and left to stand in an open vessel, the solution which is yellow at first, deposits crystals of helicin:—



Sometimes helicoidin is obtained instead of helicin, especially if the nitric acid, has a specific gravity of about 12° Bm. No gas is evolved in the reaction (except hyponitric acid), but by the further action of the nitric acid on previously formed helicin, salicylous acid is also produced. (Piria.)

b. The same mixture set aside in a closed vessel, so that the hyponitric acid cannot escape, slowly deposits between 10° and 15°:

crystals of anilotic or nitrosalicylic acid (xii, 305) the quantity of which continually increases after a week, whilst little or no more helicin is produced.



Piria regards anilotic and nitrosalicylic acids (the identity of which was assumed at vol. xii, p. 305, on the authority of Major) as distinct but isomeric acids, and likewise maintains the opinion, against Major, at a later date (*Cimento*, 2, 299; *Ann. Pharm.* 97, 254). On the other hand, Werther (*J. pr. Chem.* 76, 449), Major and Strecker (*Ann. Pharm.* 105, 299) found that the two acids are identical.

c. Salicin treated with 8 pts. nitric acid yields picric acid (xi, 211) and oxalic acid. (Braconnot.) Mixed with excess of nitric acid diluted with 10 times its bulk of water, and heated once or twice to the boiling point, it turns yellow, gives off red vapours with an odour of salicylous acid, and when left at rest, deposits that acid in the form of an oil. On again heating the liquid to the boiling point, it becomes clear, and after some time, deposits on cooling, needles of nitrosalicylic acid, which by longer boiling are converted into picric acid. (Gerhardt.)

9. In contact with *fluosilicic alcohol* (obtained by passing gaseous fluoride of silicon to saturation into absolute alcohol kept cool with ice), salicin acquires, after some time, a fine crimson colour. (W. Knop, *J. pr. Chem.* 74, 62.)

10. When a 3 p. c. aqueous solution of *osmic acid* is poured upon salicin, the latter dissolves to a colourless liquid, which even at ordinary temperatures, and more quickly when heated, becomes yellow, brown and black, from separation of osmic oxide, and emits an odour of salicylous acid, that of the osmic acid disappearing at the same time. On distilling the liquid (with further addition of osmic acid), aqueous salicylous acid is obtained, while salicylic and oxalic acids remain behind. (Buttlerow.)

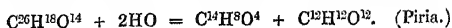
11. Salicin added by small portions to boiling *soda-ley* dissolves with effervescence, and the solution, after the alkali is saturated, deposits saliretin. On distilling the solution, after neutralising with an acid, salicylous acid passes over, and a residue is left containing salicylic acid and a brick-red powder (Bouchardat, *Compt. rend.* 19, 1179; see also below).—When salicin is added by small portions to melting *hydrate of potash*, the mass becomes brown and hot, then swells up, gives off hydrogen, and becomes colourless again. The residue contains salicylate, oxalate, and perhaps also carbonate of potash. If a sufficient excess of potash is not used, the chief products obtained are salicylous acid and a brown resin, instead of salicylic acid.—When salicin is more strongly heated with potash-hydrate, the mass blackens and gives off carbolic acid. (Gerhardt).—Salicin distilled with  $\frac{1}{2}$  pt. lime, yields Stenhouse's *salicone*, which is a mixture of carbolic and salicylous acids (Gerhardt), while charcoal and carbonate of lime remain behind.

12. *Sulphate* and *hydrochlorate* of *ferric oxide* colour salicin brown, but without forming any precipitate. The liquid when boiled becomes colourless and deposits an ochre-yellow precipitate. On evaporating the filtrate to dryness, and treating the residue with absolute alcohol, ferrous sulphate remains undissolved, and the alcohol yields by



evaporation crystals different from salicin (De Koninck, *Memoire sur la Phlorizine*, 18).

13. When salicin is brought in contact with water and *emulsin* (xii, 233) at a temperature not above 40°, it is completely resolved in the course of 10 or 12 hours, into saligenin and glucose:



Respecting the sugar thus produced, see page 348 of this volume. The transformation is not dependent on the presence of yeast; it is not prevented by prussic acid, cupric sulphate, or cyanide of mercury (Bouchardat, *Compt. rend.* 19, 602), but retarded by addition of 1 pt. caustic soda, oil of vitriol, nitric acid or hydrochloric acid to 100 pts. of the salicin, and in a less degree, if lime or magnesia be added, instead of the substances just mentioned (Bouchardat, *Compt. rend.* 20, 110). The action of *emulsin* is retarded by the presence of acetic or tannic acid (Seelheim). — When tannic acid is added to a mixture of *emulsin* and salicin, the greater part of the salicin is found unaltered at the end of 6 weeks, and partly crystallised out. The mother-liquor treated with an additional quantity of *emulsin*, and again set aside, yields, after evaporation, another portion of salicin, together with saligenin and gallic acid, but no saliretin is produced (by the action of the acids on the saligenin). (Seelheim, *Dissert.* Göttingen, 1860.) — Salicin dissolved in water, in contact with *yeast* and bicarbonate of soda, decomposes in the course of three weeks, with formation of saligenin and salicylous acid (Ranke). — 14. By digestion with *saliva*, at 38° or 40°, it is decomposed in a few hours in the same manner as by *emulsin*. The quantity of *saliva* which can be collected in a quarter of an hour is capable of decomposing 1 gramme (or more) of salicin (Städeler, *J. pr. Chem.* 72, 350; *N. J. Pharm.* 33, 127). — 15. After the ingestion of salicin, salicylous and salicylic acids are found in the urine. (Laveran & Mellon, *N. Ann. Chim. Phys.* 12, 145). After large doses, unaltered salicin is found together with saligenin, and perhaps also carbolic acid (Ranke, *J. pr. Chem.* 56, 1); (see *Handb. viii, Zoochem.* 404). Diastase does not act upon salicin at 40° (Städeler).

Salicin dissolves in cold *water*; more freely and perhaps in all proportions, in boiling water (Pelouze & J. Gay-Lussac). It dissolves in 14 pts. water at 17° (Braconnot), in 17·85 pts. at 19·5° (J. Gay-Lussac & Pelouze), in 28·57 pts. at common temperatures (Bouchardat), in 30·31 pts. at 11·5° (Piria).

It neither saturates *acids* nor combines with them. It does not undergo any alteration of rotatory power by contact with *ammonia* (Bouchardat), neither does it form a coloured compound (corresponding to phlorizin) when exposed to the air in contact with ammonia (Mulder).

It dissolves in aqueous *alkalis* more easily than in water. — When a solution of salicin in water is mixed with  $\frac{1}{2}$  pt. potash-hydrate and evaporated, there remains an uncrystallisable honey from which acids separate salicin (Braconnot): see above. — Salicin does not neutralise *lime-water* when boiled with it. Aqueous salicin does not precipitate *metallic salts*.

*Lead-compound of Salicin.* — Aqueous salicin neither dissolves lead-oxide nor precipitates neutral or basic acetate of lead. (Pelouze & Gay-Lussac.) Salicin gives

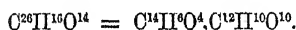
off water when heated with oxide of lead, but may be recovered unaltered by means of hydrosulphuric acid, even after being heated to 142°. (Mulder, *J. pr. Chem.* 17, 298).—The compound is obtained by adding basic acetate of lead, drop by drop, to a hot concentrated aqueous solution of salicin, till about half the salicin is precipitated, and washing the product with de-aerated water out of contact with the air.—It is a white, light powder resembling starch. Tastes sweetish and bitter. Does not give off any water when heated to 200°. It is coloured deep red by oil of vitriol, and decomposed by acids, with separation of salicin. It dissolves in potash-ley and in acetic acid. (Piria).

				Piria.	Erdmann.			
				mean.	& Marchand.			
				mean.	mean.			
26 C.....	156	....	22.35	....	21.74	.....	19.39	
14 H .....	14	....	2.01	....	2.14	.....	2.02	
10 O.....	80	....	11.46	....	13.01	.....	15.34	
4 PbO .....	448	....	64.18	....	63.11	.....	63.25	
<hr/>								
C <sup>26</sup> H <sup>14</sup> Pb <sup>4</sup> O <sup>14</sup>	....	698	....	100.00	....	100.00	.....	100.00

When aqueous salicin is mixed with *cupric sulphate* and excess of potash-ley, the precipitate formed at first dissolves to a blue liquid, which becomes turbid at a temperature below 100°, and deposits flocks which turn green, and after longer boiling, brown. (Lassaigne, *J. Chim. méd.* 181, 417.)

Salicin does not dissolve in *alcohol* more freely than in water (Braconnot). It dissolves in *acetic acid*, but is obtained in its original state on evaporating the solution to dryness (Braconnot, Hopff).—It is insoluble in *ether*.—It dissolves in cold and more abundantly in warm *creosote* (Reichenbach). It is not precipitated from its aqueous solution by *tincture of galls* or by *gelatin* (Pelouze & J. Gay-Lussac).

## Helicin.



PIRIA. *N. Ann. Chim. Phys.* 14, 287; *Ann. Pharm.* 56, 64; *J. pr. Chem.* 36, 321.

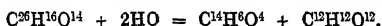
*Formation.* 1. By treating salicin with nitric acid (p. 436).—  
2. By boiling benzo-helicin with magnesia (Piria, *Ann. Pharm.* 96, 380).

*Preparation.* 1 pt. of pulverised salicin is covered with 10 pts. of nitric acid of 20° Bm., and left to stand in an open vessel, with occasional stirring, till the yellow solution, smelling of salicylous acid, which forms in about 24 hours, has re-solidified to a crystalline pulp, from formation of helicin. This pulp is freed from the mother liquor by pressure and washing with cold water; from traces of anilotic acid formed at the same time, by washing with ether; and then crystallised from boiling water.

*Properties.* Anhydrous helicin, obtained by heating the crystallised compound to 100°, melts at about 175° to a transparent liquid,

resembling palm-oil in colour and consistence, and solidifies in a crystalline mass on cooling. — Inodorous. Tastes slightly bitter, somewhat like salicin. Neutral.

*Decompositions.* 1. Helicin, melted for some time over the oil-bath, gives off water and salicylous acid, the residue thereby becoming more fusible, and ultimately solidifying on cooling, though not immediately, to a yellow opaque resin. This resin is nearly insoluble in boiling water and in alcohol, still exhibits with potash the reaction of helicin, and, when boiled with very dilute hydrochloric acid, is partially decomposed, with evolution of salicylous acid, the greater part, however, reappearing when cold as crystallised helicin. — 2. The solution of helicin in *nitric acid* of 13° or 20° Bm., set aside over-night, is found to contain a large quantity of salicylous acid. — 3. *Bromine* converts helicin into bromohelicin. Aqueous and alcoholic helicin are converted by *chlorine* into  $\alpha$ - and  $\beta$ -chlorohelicin. — 4. *Oil of vitriol* colours helicin orange-yellow, and then dissolves it. — 5. When helicin is boiled with very dilute sulphuric or hydrochloric acid, salicylous acid is given off and glucose remains in solution. A similar but weaker and less complete decomposition is produced by *oxalic, citric and tartaric acids*. — 6. When helicin is heated with *potash* or *soda-ley* the solution turns yellow from formation of salicylite of potash, and the helicin is completely decomposed. *Baryta* and *lime* act in a similar manner; *ammonia* and the *alkaline carbonates* less strongly. — 7. By aqueous *emulsin*, helicin is resolved into salicylous acid and glucose. By distilling the mixture for some hours, the whole of the salicylous acid is obtained which the helicin is capable of yielding, and the solution filtered from the coagulated emulsin contains the sugar:



8. A mixture of helicin with *yeast* which has stood for some hours, contains salicylous acid, and gives off gas when shaken.

*Combinations.* With *Water*. — *Crystallised Helicin*. Slender white needles grouped in tufts and radiate masses. Between 100° and 113° it gives off, on the average, 4.17 per cent. of water (calc. 4.54 p. c.).

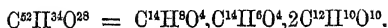
<i>Crystals.</i>				Piria. <i>mean.</i>
52 C .....	312	...	52.44	52.36
35 H .....	35	...	5.88	6.03
31 O .....	248	...	41.68	41.61
<hr/> 2(C <sup>26</sup> H <sup>16</sup> O <sup>14</sup> ) + 3aq. ....				<hr/>
	595	...	100.00	100.00

Crystallised helicin dissolves in 64 pts. *water* at 8°, and very easily in boiling water.

It does not unite with *bases*, but potash and soda increase its solubility in water. The aqueous solution has no action on *chloride of barium, chloride of calcium, zinc-salts, nitrate or acetate of lead, basic acetate of lead, sesquichloride of iron, cupric salts, corrosive sublimate or nitrate of silver*.

It is more soluble in *alcohol* than in water, but insoluble in *ether*.

## Helicoïdin.



PIRIA. *Ann. Pharm.* 56, 69; *N. Ann. Chim. Phys.* 14, 292.

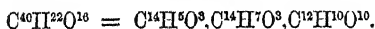
Formed by dissolving salicin in nitric acid of 12° B. (therefore also instead of helicin when the acid used for the preparation of that substance is too weak) and crystallises from the solution after some days. — Needles similar to helicin, which may be obtained pure by washing with cold water and one recrystallisation from boiling water.

Crystals.				Piria. mean.
52 C .....	312	...	52.26	52.33
37 H .....	37	...	6.19	6.30
31 O .....	248	...	41.55	41.37
<hr/> C <sup>52</sup> H <sup>34</sup> O <sup>28</sup> + 3aq. ....				
	597	...	100.00	100.00

Helicoïdin may be regarded as imperfectly oxidised salicin, but not as a mixture of salicin and helicin, inasmuch as such a mixture would not produce saligenin with alkalis.

Helicoïdin is converted by *emulsin* into glucose, salicylous acid and saligenin. On distilling it after decomposition, salicylous acid passes over, whilst glucose and saligenin crystallise from the concentrated residuc. — By *alkalis* and *acids*, it is decomposed in the same manner as by *emulsin*; in the latter case, however, saliretin is obtained instead of saligenin. In other respects helicoïdin behaves like helicin.

## Populin.



II. BRACONNOT. *Ann. Chim. Phys.* 44, 296; *Pogg.* 20, 47; *N. Tr.* 23, 2, 261; *Br. Arch.* 36, 226; *Schw.* 61, 197; *Repert.* 36, 280; *Berz. Jahresber.* 11, 286. — *J. Chim. méd.* 7, 21.

HERBERGER. *Repert.* 55, 214.

DE KONINCK. *Rev. Scient.* 1, 332.

PIRIA. *Compt. rend.* 34, 138; *N. Ann. Chim. Phys.* 34, 278; *Ann. Pharm.* 81, 245; *J. pr. Chem.* 55, 321; *Pharm. Centr.* 1852, 151; *Chem. Soc. Qu. J.* 5, 8. — *Cimento*, 1, 198; abstr. *Ann. Pharm.* 96, 375; *J. pr. Chem.* 67, 274; *N. Ann. Chim. Phys.* 44, 366; *Lieb. Kopp. Jahresber.* 1855, 688.

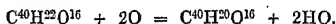
*Benzoyl-salicin.* — Discovered, in 1831, by Braconnot; investigated especially by Piria.

*Occurrence.* In the bark and leaves of the aspen, *Populus tremula* (Braconnot). Also in the root. (Van de Ghejn.) On a peculiar substance from the bark of *Populus nigra*, see Herberger (*Repert.* 55, 248); on a substance from poplar-buds, see p. 444.

*Preparation.* 1. The aqueous decoction of the bark is precipitated with basic acetate of lead; the filtrate is freed from lead by sulphuric acid, then concentrated and boiled with animal charcoal; and the salicin is left to crystallise out. The mother-liquor yields with carbonate of potash, a white precipitate of populin, which must be recrystallised from boiling water (Braconnot). Herberger, after precipitating with basic acetate of lead, removed the lead by passing carbonic acid into the liquid, and evaporated the filtrate to a syrup, from which the populin crystallised.—From the decoction of the root-bark, populin crystallises after concentration (even without precipitation by basic acetate of lead). (Van de Ghejn.)—2. The leaves of the aspen are boiled with water; the decoction is precipitated hot with basic acetate of lead; the populin carried down with the precipitate is dissolved out by boiling water; and the filtrate is evaporated to a syrup. The crystalline mass which separates is pressed between linen, heated to boiling with 60 pts. water and a little animal charcoal, and filtered at the boiling heat: the populin crystallises on cooling (Braconnot).

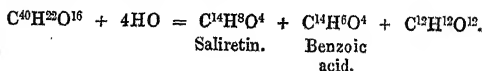
*Properties.* Crystallised populin (see below) is rendered anhydrous by heating it to 100°. Anhydrous populin melts at 180° to a colourless oil, which solidifies in a vitreous mass on cooling (Piria). Tastes sweet (Braconnot). Rotatory power, to the left, proportional to the quantity of salicin produced by the decomposition of the populin. (Biot & Pasteur, *Compt. rend.* 34, 607.)

*Decompositions.* 1. Fused populin heated to 180° gives off pungent vapours which condense in needles; at 220° it turns brown, but is obtained unaltered after solution in aqueous alcohol (Piria). When subjected to dry distillation it swells up and yields empyreumatic oil, from which benzoic acid crystallises on cooling (Braconnot).—2. It burns with flame and an empyreumatic resinous odour (Braconnot).—3. Heated with sulphuric acid and *bichromate of potash* it gives off large quantities of salicylous acid (Piria).—4. By solution in *nitric acid* of sp. gr. 1.30, it is converted into benzo-helicin, which crystallises after standing for some time. The solution at the same time is coloured yellow by hyponitric acid:



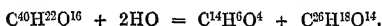
In this reaction also, the saligenin of the populin is converted into salicylous acid (Piria). Weak nitric acid acts upon populin only at the boiling heat, salicylous acid being given off from the acid solution; ordinary nitric acid acts violently, producing yellowish crystals, probably consisting of picric, nitrobenzoic and oxalic acids (Piria). Braconnot obtained nothing but picric acid; Koninck obtained picric and oxalic acids.—5. With *oil of vitriol* populin forms a deep red solution whence water throws down a red powder (Braconnot's rutilin, p. 434), which, after the sulphuric acid has been removed, dissolves in water with red colour, and is reprecipitated by acids (Braconnot). Hot oil of vitriol carbonises populin (Koninck).

By boiling with dilute acids, populin is resolved into saliretin (xii, 231), benzoic acid and glucose:



The saliretin is produced by the further action of the acid on the saligenin (xii, 234), which is the first-formed product (Piria). Concentrated *phosphoric acid* forms saliretin even in the cold (Braconnot). The formation of glucose was first observed by De Koninck.

6. Populin heated to 100° in a sealed tube with alcoholic *ammonia*, yields salicin, benzamide and benzoic ether. Gaseous ammonia does not act on populin at 150° (Piria). — 7. Heated with *potash-hydrate*, it yields oxalate of potash (Braconnot). — 8. Populin boiled with *hydrate of baryta* or of *lime*, yields a benzoate and salicin :



100 pts. crystallised populin yielded 28.9 pts. benzoic acid, the calculated quantity being 28.64 pts. (Piria). — 9. By prolonged contact with water, putrid *casein*, and carbonate of lime, it is decomposed with formation of saligenin, lactate of lime and benzoate of lime (Piria).

Populin is not altered by *chlorine* or *iodine*, or by boiling with *phosphorus* and water (Braconnot), or by *emulsin* (Piria).

*Combinations.* — With *Water*. A. *Crystallised Populin.* — White silky, very light needles (Braconnot), resembling starch or magnesia (Piria). Interlaced needles, which sometimes become broad, and appear like laminae; but always run out into a needle-shaped summit (Biot & Pasteur). Gives off water between 35° and 40°, and the rest below 100°, in all 8.43 p. c. (Piria), 4 at. = 8.45 p. c. De Koninck describes three-sided laminae which give off 5.43 p. c. water in drying.

	<i>Crystallised.</i>			<i>Piria. mean.</i>	
40 C .....	240	...	56.34	.....	56.44
26 H .....	26	...	6.10	.....	6.27
20 O .....	160	...	37.56	.....	37.29
<hr/>					
$\text{C}^{40}\text{H}^{22}\text{O}^{16}, 4\text{HO}$ .....	426	...	100.00	.....	100.00

B. *Aqueous Solution.* — Crystallised populin dissolves in about 2,000 pts. of cold water (Braconnot), in 1896 pts. at 9° (Piria), and in 70 pts. boiling water (Braconnot). The cold solution deposits populin on being saturated with common salt; the solution saturated at the boiling heat deposits it on cooling.

Populin dissolves easily and without decomposition in cold *acids* not too concentrated, and is precipitated partially by water, completely by alkalis (Braconnot, Koninck). According to Koninck, it dissolves also in aqueous alkalis, and is precipitated by acids.

Aqueous populin does not precipitate any *metallic salt*. (Braconnot.) It crystallises unaltered from solution in aqueous metallic salts, but may be made to combine with *oxide of lead*, forming a white substance insoluble in water. (Koninck.)

Populin dissolves easily in cold concentrated *acetic acid*, and is precipitated therefrom partially by water, completely by *alkalis*. (Braconnot.) It dissolves at 14°—15°, in 100 pts. absolute *alcohol* (Biot & Pasteur); in boiling alcohol more abundantly than in boiling water, scarcely at all in *ether*.

*Appendix to Populin.***Peculiar Body from Poplar-buds.**

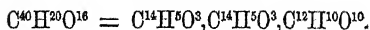
W. HALLWACHS. *Ann. Pharm.* 101, 372; abstr. *J. pr. Chem.* 71, 117; *Chem. Centr.* 1857, 401.

The bruised buds of *Populus nigra* or *P. dilatata* are boiled with water, the liquid strained, concentrated to a third, strongly supersaturated with hydrochloric acid, and left to itself for 24 hours. The separated yellow-brown mass is washed with cold water, recrystallised by repeated boiling with water, then dissolved in boiling water, and precipitated with neutral acetate of lead. The washed lead-salt is decomposed by hydrosulphuric acid under water; the solution is heated to the boiling point and filtered; and the laminæ, which separate on cooling, are purified by recrystallisation from ether or from water.

White laminæ with a silky lustre. Tasteless, with a faint odour. Melts at 180°. Has a strong acid reaction.—Contains, on the average, 62.50 p. c. C., 5.87 H., and 31.63 O.

Decomposes when heated above 200°, diffusing aromatic vapours.—Dissolves in oil of vitriol, with straw-yellow colour, changing to deep crimson on addition of a small quantity of nitric acid.—Decomposed by heating with dilute hydrochloric acid or baryta-water, with formation of sugar.—Nitric acid converts it into picric acid.—Heated with a strong solution of chloride of zinc, it assumes a violet-red colour.

Dissolves at 22° in 1998 pts. of cold water, more easily in boiling water.—Easily soluble in aqueous alkalis, also in hot alcohol; dissolves in 44 pts. ether at 22°.

**Benzo-helicin.**

PIRIA. *Ann. Pharm.* 81, 246; 96, 379.

*Formation, p. 442.*

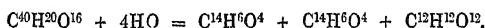
When populin is immersed in 10 or 12 pts. nitric acid of sp. gr. 1.30, the liquid in a few minutes assumes a yellow colour, takes up all the populin, and soon afterwards deposits crystals of benzo-helicin; a further quantity may be obtained by diluting the mother-liquor with water. Purified by recrystallisation from boiling water. (See below.)

*Properties.* Silky needles grouped in tufts, and not giving off any water when heated.

					Piria. mean.
40 C	240	....	61·86	.....	61·80
20 H	20	....	5·15	.....	5·23
16 O	128	....	32·99	.....	32·97
<hr/>					
$C^{40}H^{20}O^{16}$	388	....	100·00	.....	100·00

Related to helicin (p. 439), in the same manner as populin to salicin.

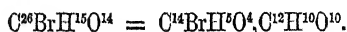
*Decompositions.* 1. The yellow solution of benzohelicin in *oil of vitriol* becomes colourless on dilution with water, and gives off the odour of salicylous acid. Salicylous acid is likewise volatilised on boiling benzohelicin with *hydrochloric acid*, and the liquid, on cooling, yields crystals of benzoic acid. In this reaction the benzohelicin is resolved into benzoic acid, salicylous acid, and glucose, according to the equation :



2. The solution of benzohelicin in *caustic alkalis* becomes golden yellow on boiling, and on addition of acids, deposits salicylous and benzoic acids, retaining glucose in solution. — 3. When benzohelicin is boiled with *magnesia* (or other bases which do not act upon helicin) benzoate of magnesia and helicin (p. 439) are obtained. It is not altered by emulsin.

Benzohelicin dissolves in boiling water. If the first drops of a solution filtered at the boiling heat crystallise on cooling, the crystallisation extends through the entire mass; but on again applying heat, and leaving the solution to cool slowly and quietly, it does not yield crystals, but solidifies to a pulpy jelly.

## Bromhelicin.



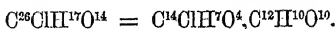
PIRIA. *N. Ann. Chim. Phys.* 14, 298; *Ann. Pharm.* 56, 72.

Prepared like chlorhelicin (p. 446), but always obtained in the form of a hydrated jelly, which dries up to a dirty white amorphous powder, giving off 2 at. water at 100°.

					Piria.
<i>Hydrated.</i>					
26 C	156	.....	40·94	.....	41·12
Br	80	.....	20·99	.....	20·71
17 H	17	.....	4·46	.....	4·57
16 O	128	.....	33·61	.....	33·60
<hr/>					
$C^{26}BrH^{15}O^{14} + 2aq.$	381	.....	100·00	.....	100·00



## Chlorosalicin.



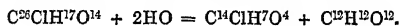
PIRIA. *N. Ann. Chim. Phys.* 14, 275; *Ann. Pharm.* 56, 52; *J. pr. Chem.* 36, 321.

*Formation*, p. 434.

*Preparation.* Chlorine gas is passed through a pulp of 1 pt. finely powdered salicin and 4 pts. water, till the whole is dissolved and a copious crystalline precipitate is subsequently formed. The separated chlorosalicin is pressed between linen, washed with a small quantity of cold water, dried between paper, freed from a small quantity of adhering resin by agitation with ether, and recrystallised from boiling water.

*Properties.* Crystallised chlorosalicin is dehydrated by a heat of  $100^\circ$  to  $110^\circ$ , and melts at a higher temperature to a colourless liquid. Inodorous. Tastes bitter, like salicin.

*Decompositions.* 1. When heated above its melting point, it gives off a large quantity of hydrochloric acid and leaves charcoal. — 2. It dissolves in oil of vitriol, with reddish colour. — 3. By dilute acids it is completely resolved into glucose and a yellow resinous precipitate, probably chlorosaliretin. — 4. Its aqueous solution is quickly decomposed by emulsin into glucose and chlorosaligenin (xii, 293):

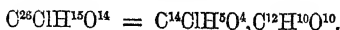


*Combinations.* — With Water. — *Crystallised Chlorosalicin.* Long, silky, very light needles, which give off 10.14 p. c. water (calc. 4 at. = 10.10 p. c.) between  $100^\circ$  and  $110^\circ$ .

	Crystals.			Piria.
				mean.
26 C .....	156.0	.....	43.76	..... 43.56
Cl .....	35.5	.....	9.96	..... 9.96
21 H .....	21.0	.....	5.89	..... 6.14
18 O .....	144.0	.....	40.39	..... 40.34
<hr/>				
$\text{C}^{26}\text{ClH}^{17}\text{O}^{14} + 4\text{aq.}$ ....	356.5	.....	100.00	..... 100.00

Chlorosalicin dissolves in water and in alcohol, but not in ether.

## Chlorhelicin.



PIRIA. *N. Ann. Chim. Phys.* 14, 295; *Ann. Pharm.* 56, 72.

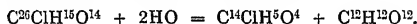
Obtained in two modifications, known as  $\alpha$ - and  $\beta$ -chlorhelicin.

*α-Chlorhelicin.* A mixture of water and helicin is shaken up in a bottle filled with chlorine gas, as long as the chlorine continues to be absorbed and hydrochloric acid formed. The helicin swells up to a transparent jelly, which must be pressed between linen, washed with cold water, and recrystallised from boiling water. The solution, on cooling, either deposits small needles of mono-hydrated *α*-chlorhelicin, or solidifies to an amorphous, pasty jelly, containing more water than the needles.

The needles, heated to between 120° and 130°, are converted into anhydrous *α*-chlorhelicin. — Inodorous. Tastes bitter.

Between 120° and 130°.					Piria.
26 C	.....	156.0	....	48.98	..... 49.02
Cl	.....	35.5	....	11.14	..... 11.02
15 H	.....	15.0	....	4.72	..... 4.90
14 O	.....	112.0	....	35.16	..... 35.06
$C^{26}ClH^{15}O^{14}$ ...					318.5 .... 100.00 ..... 100.00

*α*-chlorhelicin, when heated, gives off vapour of chlorosalicylous acid (xii, 294). The same acid is obtained, together with glucose or its products of decomposition, on heating *α*-chlorhelicin with dilute acids, or alkalis, or by treating it with *emulsin*:

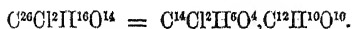


Crystallised *α*-chlorhelicin contains 3 p. c. *water*, which goes off when the crystals are heated, the quantity evolved being rather more than 1 at. (calc. 2.76 p. c. HO), probably because a small quantity of gelatinous *α*-chlorhelicin is likewise present (Piria).

Nearly insoluble in cold, easily soluble in hot *water* and *alcohol*.

*β-Chlorhelicin.* When chlorine gas is passed through an alcoholic solution of helicin, the liquid becomes hot, and deposits a white starch-like powder, an additional quantity of which is obtained on cooling. This powder contains, on the average, 48.75 p. c. C., 5.04 H., 11.46 Cl., and 34.16 O., like *α*-chlorhelicin; but it is insoluble in water, nearly insoluble in boiling alcohol, and when treated with acids, alkalis, or *emulsin*, yields neither sugar nor chlorosalicylous acid.

## Bichlorosalicin.

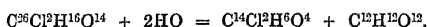


PIRIA. *Ann. Pharm.* 56, 55.

*Preparation.* Pulverised chlorosalicin is suspended in water, and chlorine is passed through it,—or chlorine gas is made to act for a considerable time on salicin (suspended in water). The product is purified by washing with ether, and recrystallisation from boiling water.

By drying at 100° the crystals are converted into anhydrous bichlorosalicin, which, at a stronger heat, melts to a transparent mass, solidifying in the vitreous form on cooling. Inodorous. Tastes rather bitter. Neutral.

*Decompositions.* 1. Bichlorosalicin, when strongly heated, gives off inflammable vapours and leaves charcoal. By *dry distillation* a heavy oil is obtained, together with an acid liquid, which yields chlorosalicylous acid when treated with ether. The chlorosalicylous acid results from the decomposition of bichlorosaligenin:  $C^{14}Cl^2H^6O^4 = C^{14}ClH^5O^4 + HCl$  (Piria).—2. When  $\frac{1}{2}$ chlorine gas is passed through bichlorosalicin suspended in water; the bichlorosalicin dissolves on applying heat to the liquid, and afterwards a red resin is precipitated. The latter is also produced, together with glucose, on heating bichlorosalicin with dilute acids, and appears to consist of bichlorosaliretin.—3. Bichlorosalicin dissolves without colour in *oil of vitriol*.—4. After being left for some time in contact with aqueous *emulsin*, it forms glucose and bichlorosaligenin (xii, 297), which, however, is produced only so long as the liquid is capable of taking it up, and only in small quantity on account of its sparing solubility:



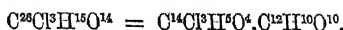
*Combinations.* With *Water*. *Crystallised Bichlorosalicin*. Long, snow-white needles, having a silky lustre: they give off at  $100^\circ$ , from 4.95 to 5.04 p. c. water (2 at. = 4.84 HO).

<i>Crystals.</i>				<i>Piria.</i> <i>mean.</i>
26 C .....	156	.....	41.82	..... 41.65
2 Cl .....	71	.....	19.03	..... 18.95
18 H .....	18	.....	4.82	..... 5.10
16 O .....	128	.....	34.33	..... 34.30
<hr/>				
$C^{26}Cl^2H^{16}O^{14} + 2aq.$ ....	373	.....	100.00	..... 100.00

Crystallised bichlorosalicin is nearly insoluble in cold, sparingly soluble in boiling *water*. It dissolves more easily in *alkaline water*, and is precipitated without alteration by acids. The aqueous solution does not act on *metallic salts*, especially not on *sesquichloride of iron*.

Soluble in *alcohol*, nearly insoluble in ether.

### Perchlorosalicin.



PIRIA. *N. Ann. Chim. Phys.* 14, 281; *Ann. Pharm.* 56, 58.

*Preparation.* When chlorine gas is passed into water at  $80^\circ$ , in which bichlorosalicin is suspended, pieces of marble being also introduced to prevent the decomposing action of the hydrochloric acid produced in the reaction, impure perchlorosalicin is precipitated in the form of a crystalline powder. This product is washed by agitation with ether, and recrystallised from hot aqueous alcohol.

The small yellowish needles, which might perhaps be obtained colourless by repeated crystallisation, become anhydrous at  $100^\circ$ , and melt at a stronger heat. Inodorous. Tastes somewhat bitter.

*Decompositions.* Perchlorosalicin decomposes at a strong heat.—

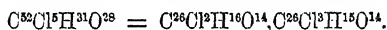
With dilute *acids* it yields a resin, probably perchlorosaliretin. — In contact with solution of *emulsin* under water, it yields, after a while, a liquid which colours ferric salts blue, but only a very small quantity of perchlorosaligenin is set free.

*Combinations.* With *Water*. — *Crystallised Perchlorosalicin* (see above) heated to 100° in a current of air gives off 4.48 p. c. water (2 at. = 4.43 p. c. HO).

<i>Crystals.</i>				Piria. <i>mean.</i>
26 C .....	156.0	....	38.87	.... 38.15
3 Cl .....	105.5	....	25.46	.... 26.00
17 H .....	17.0	....	4.18	.... 4.36
16 O .....	128.0	....	31.49	.... 31.49
<hr/>				
C <sup>26</sup> C <sup>3</sup> H <sup>15</sup> O <sup>14</sup> + 2HO				406.5    .... 100.00    .... 100.00

Nearly insoluble in cold, and very slightly soluble in boiling *water*; more soluble in weak *spirit*.

### Compound of Bichlorosalicin with Perchlorosalicin.

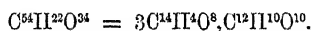


PIRIA. *Ann. Chim. Phys.* 69, 323; *N. Ann. Chim. Phys.* 14, 283.

Piria formerly obtained this compound, in an impure state, by passing chlorine gas for a long time into water containing salicin in suspension, as a yellow, pearly, crystalline mass; he now regards it as a mixture of bi- and per-chlorosalicin.

				Piria. <i>mean.</i>
52 C .....	312.0	.....	41.91	..... 42.08
5 Cl .....	177.5	.....	23.84	.... 22.97
31 H .....	31.0	....	4.16	..... 4.31
28 O .....	224.0	.....	30.09	..... 30.64
<hr/>				
C <sup>52</sup> Cl <sup>15</sup> H <sup>31</sup> O <sup>28</sup> .....				744.5    ..... 100.00    ..... 100.00

### Gallo-tannic or Tannic Acid.



DEVEUX. *J. Phys.* 42, 401.

SEGUIN. *J. des Arts et Manuf.* 2, 66, and 3, 71; *Ann. Chim.* 20, 15.

BARTHOLDI. *Schw. J.* 8, 294.

VAUQUELIN. *Ann. Chim.* 46, 321.

KARSTEN. *Schw. J.* 7, 472.

CADET. *Ann. Chim.* 4, 405; *N. Tr.* 3, 1, 480.

H. DAVY. *A. Gehl.* 4, 343.

SERTÜNER. *Schw.* 4, 410.

BERZELIUS. *Ann. Chim.* 94, 318. — *Scher. Ann.* 1, 421; *Pogg.* 10, 257. *Lehrbuch*, 3 Aufl. 6, 213.

- GIESE. *Scher. Ann.* 1, 459.  
 A. VOGEL. *Taschenb.* 1820, 74.  
 C. G. GMELIN. *Taschenb.* 1820, 100.  
 PELLETIER & CAVENTOU. *Ann. Chim. Phys.* 15, 337.  
 PFAFF. *Schw.* 52, 324.  
 GEIGER. *Mag. Pharm.* 25, 1, 99; 25, 3, 91.  
 PELOUZE. *J. Chim. méd.* 10, 257; *Pogg.* 38, 29; *Ann. Chim. Phys.* 54, 337; *Ann. Pharm.* 10, 145; *J. pr. Chem.* 2, 301. — *Ann. Pharm.* 10, 210; *J. pr. Chem.* 2, 320. — *Ann. Chim. Phys.* 56, 303.  
 BÜCHNER. *Repert.* 46, 316.  
 LIEBIG. *Ann. Pharm.* 10, 172; *J. pr. Chem.* 2, 321. — *Ann. Pharm.* 26, 128, and 162. — 39, 97.  
 GUTHOURT. *Rev. scient.* 13, 32; abstr. *Ann. Pharm.* 48, 359.  
 ROBIQUET. *Ann. Chim. Phys.* 64, 385; *J. Chim. méd.* 13, 209; *Ann. Pharm.* 25, 151; *J. pr. Chem.* 11, 481.  
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 WITTESTEIN. *Repert.* 95, 289, and 96, 215. — *Pharm. Vierteljahr.* 2, 72.  
 WETHERILL. *N. J. Pharm.* 12, 107; *J. pr. Chem.* 42, 247; abstr. *Pharm. Centr.* 1847, 749.  
 MULDER. *Scheik. Onderz.* 4, 639; abstr. *J. pr. Chem.* 48, 90.  
 STRECKER. *Ann. Pharm.* 81, 248; *Chem. Soc. Qu. J.* 5, 102; abstr. *Pharm. Centr.* 1852, 427. — *Ann. Pharm.* 90, 328; abstr. *J. pr. Chem.* 62, 434; *Pharm. Centr.* 1854, 753; *N. Ann. Chim. Phys.* 42, 231; *Phil. Mag.* [4], 8, 157.  
 A. & W. KNOP. *J. pr. Chem.* 56, 327; *Pharm. Centr.* 1852, 417; abstr. *Ann. Pharm.* 84, 283.  
 E. ROBIQUET. *N. J. Pharm.* 23, 241; abstr. *Compt. rend.* 35, 19; *J. pr. Chem.* 57, 127. — *N. J. Pharm.* 26, 29; *J. pr. Chem.* 62, 419.  
 W. KNOP. *Pharm. Centr.* 1854, 855; 1855, 657 and 737; 1856, 513; 1857, 370; 1860, 278.  
 ROCHLEDER & KAWALIER. *Wien. Akad. Ber.* 29, 28; 30, 159; *J. pr. Chem.* 74, 28 and 399; *Chem. Centr.* 1858, 579; *Chem. Gaz.* 1858, 421.

*Tannin, Tannin principle, Gerbstoff, Gerbendes Princip, Lohstoff, Eichengerbstsäure* (Berzelius). — Recognised as a distinct substance by Deveux; more exactly by Seguin; first prepared pure or nearly pure by Berzelius; shown to be a glucoside (p. 341) by Strecker.

*Sources.* In Turkish gall-nuts (*Handb.* viii, *Phytochem.* 77), in ordinary oak-apples and Chinese gall-nuts [excrecences formed on the branches of *Rhus semialata* or *R. Chinensis*. (Schenk, *N. Repert.* 5, 26 and 346.)]

Many other plants and parts of plants contain substances, mostly amorphous, which have a slight acid reaction, and a rough, but not sour taste, precipitate gelatin and albumin from their solutions, and unite with animal membrane into a mass which resists putrefaction, namely, leather, the skin then becoming tanned. All these substances, the tannic acids, were at first supposed to be identical with gallo-tannic acid, or to differ from it only in consequence of the admixture of foreign matters. In the third edition of this Handbook, a distinction was made between tannin which gave a blue, and tannin which gave

a green colour with ferric salts (see below); but this distinction has lost its value since the discovery of a number of distinct tannic acids existing in nature. The more exactly investigated bodies of this group will be separately treated in an *Appendix to Gallo-tannic acid*, their formulæ not being sufficiently well established to enable us to assume their exact places in the general system. Moreover, the researches hitherto published do not enable us to determine with certainty, which of these acids may correspond to gallic or to ellagic acid (that is to say to the products of decomposition of gallo-tannic acid). (Kr.)

On the validity of the distinction between *iron-blueing* and *iron-greening* tannin, several views have been put forward, in which, however, these denominations have been understood as applying to two groups of bodies. If, according to Geiger, water containing a small quantity of alkali be gradually added to a ferric salt which has been turned green by any kind of iron-greening tannin, the green colour changes to violet-black, the tint usually produced by iron-blueing tannin. On adding an acid, the green colour is restored. — According to this result, the difference between the two groups might be that the iron-blueing tannin is less rich in free acid; nevertheless, it reddens litmus more strongly than the other kind of tannin. It appears to contain [?] to be capable of yielding] a larger proportion of gallic acid; but iron-blueing tannin is not converted into the iron-greening kind by addition of gallic acid. (Gmelin.) — The blue or green reaction is by no means an infallible characteristic of the species of tannic acid, since bases colour the ferric compounds of tannic acid blue, and acids change the blue to green. With ferric acetate, the iron-greening acids form a blue compound; the green compound which they form with other ferric salts, is turned blue by addition of a sufficient quantity of acetate of lead, either neutral or basic, and even by a large quantity of gelatin. A compound of iron-greening tannic acid with lead-oxide, is turned blue by ferric sulphate; an iron-greening tannic acid is turned blue by continued exposure to the air, in contact with water and iron-turnings. (Cavallius, *Berz. Jahresh.* 1841, 274.) But the colours thus obtained with iron-greening tannic acids are very different from those produced by the iron-blueing acids, and the two cannot be converted one into the other. Thus, catechu-tannic acid (obtained by exhausting catechu with a small quantity of water: see below) left in contact for a few days with iron filings, assumes a dirty greyish, not a black-blue colour, and the precipitate does not turn green when treated with a small quantity of acetic acid, but dissolves on the addition of a larger quantity, and is precipitated purple-grey on addition of ammonia. The iron-greening tannic acids of catechu, kino, alder, larch, and birch-bark, and of tormentilla-root, are likewise incapable of yielding a good ink. The extracts of iron-greening parts of plants do not yield pyrogallic acid by dry distillation, unless they contain gallic acid ready formed. (Stenhouse.) This also shows the incorrectness of the view advanced by Hennig (*N. Br. Arch.* 73, 150), who regards the two groups as not essentially different from gallotannin, and as identical therewith when pure.

All iron-greening tannic acids (as those from kino, tormentilla and bistorta roots) yield pyrocatechin (xi, 379) by dry distillation, whereas the iron-blueing acids yield pyrogallic acid (xi, 398). Many plants contain both iron-blueing and iron-greening tannin; and these yield, by fractional precipitation with sugar of lead, first iron-blueing and after-

wards iron-greening precipitates. This is the case with tormentilla and bistorta roots, both of which yield at first an aqueous extract, which turns ferric salts blue, but after incomplete precipitation with sugar of lead, turns them green (Eissfeldt, *Ann. Pharm.* 92, 109; Uloth, *Ann. Pharm.* 111, 215).

Tannic acids occur especially in perennial plants, but are likewise found in annuals and biennials (Wahlenberg). Pettenkofer (*N. Repert.* 3, 74), found tannic acid in *Solanum tuberosum* and *Potentilla tormentilla*, which are perennial, but not in the annual species, *Solanum tuberosum* [*S. Dulcamara* or *S. nigrum*] and *Potentilla anserina*.—Tannic acids are found in the perennial roots of annual species, in the bark of most tree-stems, and in the young branches of shrubs and woody plants. The white inner part of the bark, lying next to the alburnum, contains the purest tannic acid, whilst the middle portion contains more extractive matter, and the outer bark is generally destitute of both; young barks contain more tannic acid than older barks, in which, indeed, they are for the most part converted into brown extractive matters (Davy). Tannic acids are also found in the husks of fruits and seeds, and in unripe fruits, less frequently in the leaves, and least of all in the petals. According to Wahlenberg, they are never found in the interior of the seed, or in poisonous plants, or in such as contain caoutchouc or milky juice.

*Iron-blueing tannic acids* are found in the leaves, bark, &c., of the oak, poplar, birch, hazel-nut, and other trees; the leaves of *Arbutus Uva ursi* and *Arbutus Unedo*, *Lythrum salicaria*, the stalks of *Ribes rubrum*, the bark of *Cornus mascula*, and many other plants and vegetable organs.—*Iron-greening tannic acids* occur in catechu, cinchona-barks, pines and firs, in the root of *Crameria triandra*, *Rheum Rapaonticum*, tormentil,—in the bark of *Salix triandra* and *S. undulata*, of *Alnus glutinosa*, *Pinus Larix* and *Rhizophora Mangle*, the common black mangrove (Stenhouse), and many other plants.

The tannic acid of the *Sumach* is identical with, or very similar to, gallo-tannic acid. It yields pyrogallic acid by dry distillation, and gallic acid when decomposed by sulphuric acid. (Stenhouse.)—Black tea contains a small quantity of boheic acid (xii, 473), and a very large quantity of gallo-tannic acid. The aqueous infusion precipitated with sugar of lead yields a salt, the organic substance of which contains 50.4 p. c. C., 4.2 H., and 45.4 O., agreeing therefore in composition with gallotannate of lead. When boiling aqueous sugar of lead is added in excess, a precipitate is formed containing 64.49 p. c. lead-oxide (Rochleder, *Ann. Pharm.* 63, 202). The aqueous extract, either of black or of green tea, yields, by dry distillation, pyrogallic acid, proceeding from the gallic acid contained in the tea. From the infusion of the tea,  $\frac{1}{2}$  vol. oil of vitriol throws down a dark brown precipitate, which dissolves in water much more easily than that from gallo-tannic acid, and does not yield any pyrogallic acid by dry distillation. When boiled with dilute sulphuric acid, it does not yield any gallic acid, but a brown substance sparingly soluble in water, and is therefore altogether different from gallo-tannin (Stenhouse). On the tannic acid of tea, see also Mulder (*Pogg.* 43, 635).—The tannic acids of *kino* and of *tormentil root*, agree when pure with gallo-tannic acid; in the impure state, they precipitate ferric chloride green or grey; in the pure state, blue-black (Hennig); see *Kinotannic acid*.—The tannic acid of *oak-bark* is regarded by Berzelius (*Lehrbuch*, 3 Aufl. 6, 213), as identical with gallotannic

acid. According to Stenhouse, it yields neither gallic nor pyrogallic acid; the precipitate produced by boiling with dilute sulphuric acid is red-brown and nearly insoluble in water.

Mirabelles, Valonia, Dividivi, the fruit of *Anacardium longifolium*, bistorta-root, pomegranate-bark, and the bark of the birch, hazel-nut and larch, contain tannic acids different from gallo-tannic acid (Stenhouse).

Turkish gall-nuts contain 65 p. c. tannic acid (Guibourt), 72 p. c. (Mohr), 55 to 60 (Büchner), Chinese gall-nuts contain 69 p. c. (Bley, Stein); Bassorah gall-nuts, 26 p. c. (Bley, *N. Br. Arch.* 75, 138).

*Preparation.* 1. A displacement apparatus is half filled with finely pulverised gall-nuts, and commercial ether containing water and alcohol is poured in. The liquid which runs away separates into two layers, the lower of which is a heavy, syrupy, amber-coloured solution of tannic acid, water and ether, while the upper is mobile, consisting of ether, water, gallic acid, and a small quantity of tannic acid. Ether is poured into the apparatus as long as the lower stratum continues to increase; the upper layer is then removed; and the lower is repeatedly washed with ether, and dried in vacuo, or by heat. Gall-nuts thus treated yield from 35 to 40 p. c. tannic acid (Pelouze). A better mode of proceeding is to stir powdered gall-nuts to a paste with commercial ether, leave it to macerate, press through linen, and exhaust the galls by repeated treatment: the product thus obtained amounts to 60 per cent. (Lecannot, *J. Pharm.* 22, 149; *Ann. Pharm.* 18, 179. — Dominé, *N. J. Pharm.* 5, 231). The latter uses commercial ether of 56° Baumé, and leaves the gall-nut powder previously for 4 days in a cellar, so that it may absorb moisture, before submitting it to the action of the ether. The tannic acid thus obtained is somewhat less pure than that which is prepared by displacement (Béral, Mohr).

2. 100 pts. powdered gall-nuts are treated in the displacement apparatus with a mixture of 300 pts. ether, 15 pts. alcohol of 90 p. c., and 5 pts. water (or 20 pts. alcohol of 69 p. c.); the residue, after the liquid has run off, is twice treated with the same mixture, three times with pure ether; and the whole of the extracts are shaken up together, and left to settle for a week. The upper of the two layers thus formed is decanted from the syrup below; the latter is evaporated over the water-bath; and the residue is dried between 100° and 110°. The decanted ether deposits an additional quantity of syrup, if a third of it is subjected to distillation and the residue thereby obtained is mixed with the remaining two-thirds, or if a little water is added. To free the tannic acid thus obtained (or according to 1) from admixed gallic acid, ellagic acid, volatile oil, and chlorophyll, 100 pts. of it are shaken up with 100 pts. water and 200 pts. ether, whereby three layers are formed, the upper consisting of ether, the middle of aqueous gallic acid and impure tannic acid, while the lowest, which is syrupy and amounts to 215 pts., leaves, on evaporation, 90 pts. of pure tannic acid (Guibourt). — Béral, (*J. Chim. méd.* 75, 225) adds to 8 pts. gall-nut powder the half of a mixture of 12 pts. ether, 3 pts. alcohol of 85 p. c. and 1 pt. water; places the mixture in a funnel provided with a stop-cock; pours the rest of the liquid on it; leaves it to drain away for 6 hours; displaces the solution still remaining in the funnel by pouring in 4 or 5 pts. of water; and evaporates the filtered liquid. The same process is adopted by Brandes (*N. Br. Arch.* 21, 329). — Mohr employs for the extraction a mixture of



equal volumes of ether and alcohol of 90 p. c. The filtrate is syrupy, but thinner than that obtained by 1, and forms only one layer, exhibits but little turbidity on the addition of a large quantity of ether, and if 7 fluid ounces of ether are used to 2 oz. of galls, yields a quantity of tannic acid amounting to 72 per cent. of the galls. If a mixture of 4 vols. ether and 1 vol. alcohol of 90 p. c. is used, the extract has the same constitution (Molr, Sandroek).—With Chinese galls, hydrated ether acts better than ether-alcohol (E. Riegel, *N. Jahrb. Pharm.* 3, 252).

3. Four parts of gall-nut powder covered with 8 pts. water, are left to stand for two hours; the liquid is filtered; the filtrate, amounting to about 4 pts., is mixed with 2 pts. ether and poured into a tap-funnel; and the syrupy layer thus formed (containing 40 pts. tannic acid to 7 pts. water and 53 pts. ether), is separated from the upper liquid; which latter, if again agitated with ether, yields an additional quantity of syrup. By this process,  $\frac{1}{3}$  of the tannic acid contained in the decoction is obtained (Béral).

4. Aqueous extract of gall-nuts is exhausted with ether, which takes up the gallic acid together with part of the tannic acid; the solution is then evaporated; and the admixed crystals of gallic acid are dissolved out of the residue by small quantities of ether (Berzelius).

5. Gall-nut powder is exhausted with a moderate quantity of hot water, strained through linen and pressed; the turbid infusion is stirred up with a small quantity of dilute sulphuric acid, which precipitates the matters causing the turbidity, so that at last the liquid goes clear and easily through the filter; and oil of vitriol is added to the filtrate as long as the precipitated white flocks are thereby made to unite, in the course of an hour, into a brownish pitchy mass, which, in addition to tannic and sulphuric acids, contains oxidised extractive matter, and perhaps also other substances. The liquid decanted therefrom is mixed with oil of vitriol, as long as a precipitate is thereby formed; the white or yellowish flocks are thrown upon a filter, washed with water containing a sufficient quantity of sulphuric acid to prevent it from exerting a solvent action,—pressed between bibulous paper as long as they render the paper moist, and then dissolved in cold water; the solution is mixed with finely pulverised carbonate of lead as long as effervescence ensues, and placed in contact with a small quantity of carbonate of lead till it no longer precipitates chloride of barium; and the filtered liquid is immediately evaporated in vacuo. The solution in boiling water of the pitchy precipitate obtained with sulphuric acid, deposits, on cooling, a similar, but still more impure, pitchy substance; whilst purer tannic acid remains in solution, which, however, cannot be obtained quite pure by treatment with carbonate of lead, &c. (Berzelius).—Rochleder & Kawaller employ hydrochloric instead of sulphuric acid, the former, according to Stenhouse, precipitating tannic acid more completely from its aqueous solution.

6. The infusion clarified with a very small quantity of sulphuric acid and filtered, as in method 5, is mixed with aqueous carbonate of potash or carbonate of ammonia, as long as anything is thereby precipitated (if too much alkali is present, the precipitate re-dissolves); the white precipitate, containing tannate of potash or

ammonia, is washed on the filter with the smallest possible quantity of cold water, then dissolved in boiling dilute acetic acid, and the solution is left to cool, foreign matters then separating out. The liquid separated therefrom is precipitated by basic acetate of lead; the washed and still moist precipitate is suspended in water and decomposed by hydrosulphuric acid; the liquid is filtered; and the limpid filtrate is immediately evaporated in vacuo over carbonate of potash (Berzelius). — 7. Gall-nut powder is exhausted with cold water; the filtrate is nearly neutralised with ammonia, so that it retains but a slight power of reddening litmus—then precipitated by chloride of barium; the tannate of barium is left to settle down in a bottle filled with the liquid; the solution is decanted; the precipitate washed on a filter with cold water, whereby it is turned green and partially dissolved,—then dissolved in acetic acid; the liquid is filtered and precipitated by basic acetate of lead; and the precipitated tannate of lead is decomposed by hydrosulphuric acid, as in 6. (Berzelius.)

The older methods of Thomson, Grotthus (*Schw.* 13, 132), Proust (*Scher. J.* 2, 252; 10, 91), Bouillon-Lagrange, Merat-Guillot (*Scher. J.* 10, 87), Trommsdorff (*A. Gehl.* 3, 111. — *N. Tr.* 2, 1, 61. — *Paschenb.* 1820, 43), Schrader (*N. Gehl.* 8, 509), Löper (*N. Tr.* 5, 1, 339), Meissner (*Berl. Jahrb.* 29, 2, 61, and 91), yield impure tannic acid or sometimes none at all.—To obtain tannic acid from vegetable substances containing too great a proportion of foreign matters to admit of direct extraction with ether, the aqueous extract is precipitated with acetate of quinine, cinchonine, or some other vegetable alkali; the washed precipitate is dissolved in alcohol; the tannic acid is precipitated with neutral acetate of lead; the precipitate decomposed by hydrosulphuric acid; the filtrate evaporated to dryness in vacuo; the residue dissolved in ether-alcohol; and the solution again evaporated (*Gerhardt, Traité*, 3, 849).

*Purification.* By solution in ether of sp. gr. 0.72, which leaves undissolved the greater part of the yellowish brown tannic acid rendered fluid by the water in the ether (Berzelius). The ethereal solution of tannic acid (prepared by 1) is mixed with such a quantity of water as to form three layers, the lowest of which is syrupy and may be separated by a tap-funnel, this liquid is then mixed with water, and warmed till the ether or alcohol is completely expelled, then evaporated in vacuo over oil of vitriol, and the residue is dried between 120° and 130° (Strecker). From impure tannic acid, anhydrous ether extracts gallic acid, fat and resin, and likewise ellagic acid if it has been prepared with ether-alcohol. Of the three layers formed by agitation with ether and water, the middle one contains these impurities dissolved in ether (Luboldt).

Tannic acid prepared and purified by method 1, cannot be further resolved into different substances by repeatedly treating its ethereal solution with water, but exhibits the same composition before and after this treatment (Strecker). Rochleder & Kawalier, on the other hand, regard the tannic acid obtained from gall-nuts by exhaustion with ether and water, as a mixture still containing gallic and ellagic acids;—this conclusion they deduce from the following experiments:—

Turkish gall-nuts exhausted with ether and water in the displacement apparatus yield a solution which separates into three layers, the uppermost  $\alpha$  being yellowish and mobile, and containing a large

quantity of gallic acid; the lowest  $\beta$  having a brown colour and depositing a large quantity of ellagic acid, when left for some time out of contact with air, or when treated with acids; and the middle  $\gamma$  being brownish yellow and syrupy. This middle layer separated, washed with ether, mixed with water, warmed till the ether is evaporated, and then precipitated with neutral acetate of lead, yields a yellowish white precipitate; and, on treating this precipitate *a* with 50 cc. acetic acid and 200 cc. water,—the undissolved portion *b* with 100 cc. acetic acid and 200 cc. water,—and in like manner the successive undissolved portions, *c* with 150 cc. acetic acid and 150 cc. water, *d* with 200 cc. acetic acid and 100 cc. water, and *e* with 200 cc. acetic acid, five solutions *a*, *b*, *c*, *d*, *e* are obtained, together with a residue *f*. Each of these solutions is precipitated with basic acetate of lead; and the precipitates, after washing with water, are decomposed by hydrosulphuric acid, the precipitate *f* being also treated in the same manner. On filtering the solutions from the sulphide of lead, and evaporating them, first in a stream of carbonic acid, afterwards in vacuo, *a* leaves nearly pure gallic acid; *b* a mixture of gallic and tannic acid; *c* tannic acid with traces of gallic acid;—while *d* and *e* leave a transparent vitreous mass which gradually becomes opaque, perfectly white, and very friable; *f* leaves ellagic and tannic acid. *d*, dried at 100° in vacuo, contains 50·81 p. c. C., 3·86 H., and 45·33 O., and when boiled with hydrochloric acid in a stream of carbonic acid, yields 1·38 p. c. ellagic acid and 4·38 p. c. sugar; but this portion of *d*, if twice boiled in the state of powder, with quantities of ether not sufficient to dissolve it completely, and, after the removal of these somewhat coloured extracts, dissolved completely in ether, and evaporated in vacuo after addition of water, contains 51·72 p. c. C., 3·76 H., and 44·53 O., and yields with hydrochloric acid, 0·73 p. c. ellagic acid and 7·07 p. c. sugar.—*e* behaves externally like *d*.—The tannic acid of *f*, when separated from the ellagic acid, contains 52·21 p. c. C., 3·59 H., and 44·20 O., and yields with hydrochloric acid, 7·27 p. c. ellagic acid and 4·96 p. c. sugar (Rochleder & Kawalier).

*Purification according to Rochleder & Kawalier.*—The solution of tannic acid in the smallest possible quantity of water is shaken up with a small quantity of solution of neutral acetate of lead; the filtrate is mixed with water, and filtered again from the very impure tannate of lead thereby precipitated; and the new filtrate is precipitated by neutral acetate of lead in three portions. By decomposing the first and third of these precipitates with hydrosulphuric acid, and expelling the excess of that acid by a stream of carbonic acid, solutions are obtained, which, when boiled with hydrochloric acid out of contact with the air, yield a large portion of ellagic acid. If the tannic acid solution obtained in like manner from the middle portion be precipitated by tartar-emetic, with addition of a little carbonate of ammonia,—the precipitate washed with hot water and decomposed under water with hydrosulphuric acid,—and the excess of that acid expelled by passing carbonic acid into the hot liquid, the filtrate, when left to itself in vacuo, becomes turbid and deposits a brown substance. The solution separated from this substance by filtration, and evaporated in vacuo, leaves colourless amorphous tannic acid, which, when boiled with hydrochloric acid, no longer yields ellagic acid.

*Estimation of Tannic Acid in Astringents.* 1. The aqueous extract is

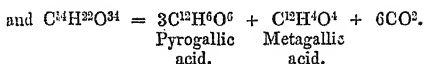
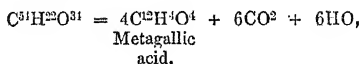
mixed with solution of gelatin, as long as a precipitate is thereby produced, the quantity of tannic acid which the same solution of gelatin (or another of known strength) is capable of precipitating, having been determined by a previous experiment. (Wheeler, *Mem. Chem. Soc.* 3, 319; Fehling, *Pharm. Centr.* 1853, 872; *Dingl.* 130, 53. — G. Müller, *Dingl.* 151, 69; *Chem. Centr.* 1859, 42.) Müller mixes the gelatin-solution with  $\frac{1}{4}$  pt. alum, to accelerate the clarification of the liquid. — To obviate the necessity of filtering, or waiting for the slow deposition of the precipitate towards the end of the experiment, Wheeler dips into the solution a glass tube loosely closed at the bottom with sponge, and tries whether the gelatin-solution which enters the tube still gives a cloud with solution of gelatin. — 2. Stein mixes the aqueous extract with a known volume of a standard solution of neutral acetate of lead, dilutes the mixture to a given volume, and determines the quantity of lead remaining in a measured portion of the filtrate. (*Schweiz. polyt. Zeitschr.* 2, 169.) — 3. Monier (*Compt. rend.* 46, 577; *Dingl.* 148, 209) mixes the aqueous extract with solution of mineral chamæleon, which rapidly decomposes tannic acid,—the quantity of tannic acid which this solution is capable of decomposing having been previously determined. — 4. Hammer (*J. pr. Chem.* 81, 159) determines the specific gravity of the solution both before and after the removal of the tannic acid, by addition of about a four-fold quantity of animal skin, which has been softened in water, pressed between linen, then washed, dried, and pulverised. See Table of the specific gravity of aqueous tannic acid (p. 463). — On the estimation of tannic acid, see also F. Müller (*N. Br. Arch.* 38, 147), Löwenthal (*J. pr. Chem.* 81, 150); Handke (*J. pr. Chem.* 82, 345; *Pharm. Viertelj.* 10, 588; *Zeitschrift für analyt. Chemie*, 1, 104); H. Sackur (*Ueber den Gerbprocess. Dissertat.* Berlin, 1860).

*Properties.* Colourless, amorphous mass remaining, when its aqueous solution is evaporated, in transparent, vitreous, shining, fissured, easily friable lumps. Inodorous. Tastes strongly astringent, but not at all bitter. Reddens litmus strongly. Does not soften between the fingers. Acquires a yellow colour by exposure to light, even in closed vessels. — No optical rotatory power. (Kr.)

				Berzelius.		Pelouze. at 120°.		Liebig. at 120°.		
54 C	.....	324	....	52.42	....	51.43	.....	50.83	....	51.50
22 H	.....	22	....	3.56	....	3.79	.....	4.20	.....	3.95
34 O	.....	272	....	44.02	....	44.78	.....	44.97	.....	44.55
<hr/>										
C <sup>54</sup> H <sup>22</sup> O <sup>34</sup>	.....	618	....	100.00	....	100.00	.....	100.00	.....	100.00
<hr/>										
				Mulder.	Wetherill. at 100°.		Van Bijlert.		Strecker. at 120°.	
C	.....	51.80	.....	50.63	.....	51.90	.....	52.25		
H	.....	3.75	.....	3.64	.....	3.75	.....	3.71		
O	.....	44.45	.....	45.73	.....	44.35	.....	44.04		
<hr/>										
				100.00	.....	100.00	.....	100.00	.....	100.00

The analyses are given in mean numbers. For Rochleder & Kawalier's analyses see page 456. Earlier formulæ: C<sup>18</sup>H<sup>8</sup>O<sup>12</sup> (Pelouze); C<sup>18</sup>H<sup>8</sup>O<sup>12</sup> (Liebig); C<sup>14</sup>H<sup>6</sup>O<sup>10</sup> (Wetherill); C<sup>28</sup>H<sup>10</sup>O<sup>18</sup> (Mulder). Strecker at first proposed the formula C<sup>40</sup>H<sup>18</sup>O<sup>28</sup>, then that above given, deduced from many accordant analyses and from the products of decomposition. Rochleder and Knop doubt its correctness.

*Decompositions.* 1. Tannic acid heated to 150° or 160°, becomes darker from incipient decomposition (Strecker); at 215° it is resolved into water, carbonic acid, and pyrogallic acid, which volatilise, and metagallic acid, which remains. At 250°, only metagallic is formed, without pyrogallic acid. (Pelouze.) The decomposition begins at 180°; at 250°, 6·5 p. c. acid water goes over, which holds the pyrogallic acid in solution, while 53—59 p. c. metagallic acid remains. Pyrogallic acid also sublimes, and the carbonic acid which escapes contains a small quantity of a gas not absorbable by potash. (Mulder.) These decompositions are represented by the equations—



The two decompositions may go on simultaneously. (Strecker.)

*Metagallic acid* (Mulder's *melangallic*, Gerhardt's *gallulmic acid*)—which is likewise produced by rapidly heating gallic acid to a temperature between 240° and 250° (xii, 401)—remains in the distillation vessel in which gallo-tannic is heated, as a black, highly lustrous, tasteless mass, and exhibits the same composition whether prepared from tannic or from gallic acid, or after solution in potash-ley and precipitation with acids,—containing, on the average, 66·15 p. c. C., 3·86 H., and 29·99 O., and answering, according to Pelouze, to the formula  $\text{C}^{12}\text{H}^4\text{O}^4$  (calc. 66·66 C., 3·70 H., and 29·64 O.). It is quite insoluble in water; dissolves easily and without residue in aqueous ammonia, potash, and soda, also in glucina (?), and is precipitated by acids. When aqueous potash is boiled to saturation with precipitated metagallic acid, the solution is neutral to vegetable colours. The acid eliminates carbonic acid from alkaline carbonates, but has no action on pure baryta or its carbonate. The potash-salt forms black precipitates with metallic salts; the silver-salt contains 53·88 p. c. AgO; 34·11 C., 1·47 H., and 10·54 O. (Pelouze).—According to Pelouze, metagallic acid, prepared by heating tannic or gallic acid, is apt to retain pyrogallic or gallic acid. When freed from these acids by heating it as long as it yields any sublimate, it contains, on the average, 66·75 p. c. C., 3·60 H., and 39·65 O.; its silver-salt obtained by mixing the ammoniacal solution of the acid with nitrate of silver, and precipitating with acetic acid, retains ammonia when dried at 140°, and has a silvery lustre. By digesting the excess of acid with potash-ley for several hours, evaporating the filtrate, and drying at 130°, the potash-salt is produced containing 12·2 p. c. KO., 58·5 C., 2·4 H., and 26·7 O. From these results, Mulder represents the acid and the potash-salt by the formulæ  $\text{C}^{10}\text{H}^{10}\text{O}^{14}$  and  $\text{C}^{10}\text{H}^{10}\text{O}^{14}, \text{KO}$ .

2. Tannic acid heated in a platinum spoon, decrepitates, undergoes semifusion, swells up, carbonises, takes fire, and burns with a bright flame, leaving an easily combustible cinder. (Berzelius).—3. Exposed on a watch-glass to strongly *oxygenised air*, it acquires a yellow or yellow-brown colour, becomes glutinous and fluid, strongly acid, from formation of oxalic acid, and if the action be continued long enough, disappears completely, being converted into water and carbonic acid. (Schönbein, *J. pr. Chem.* 81, 12).—4. Aqueous tannic acid, through which *oxygenised air* is passed, absorbs it quickly and completely, becomes dark brown-red, then again lighter, and forms oxalic acid and a substance which reduces cupric oxide, these products being decomposed by the further action of the ozone, so that the liquid ultimately leaves but little residue when evaporated. (Gorup-Besanez, *Ann. Pharm.* 110, 106). When a very dilute aqueous solution of tannic acid is exposed to the *air*, it becomes turbid, from separation of grey crystal-

line gallic acid; oxygen is absorbed at the same time, and an equal volume of carbonic acid is produced. (Pelouze.) Aqueous tannic acid, evaporated with aid of heat in open vessels, leaves a brown non-translucent mass, which, when treated with water, leaves a dark-brown residue, a further quantity of which is obtained by repeated evaporation and re-solution (Berzelius). This residue is the oxidised tannic acid of the older chemists.—*Peroxide of hydrogen* and oxygenated oil of turpentine do not produce any perceptible alteration in tannic acid. (Schönbein.)

5. Aqueous tannic acid dissolves finely divided *iodine*. (Debauque, *N. Br. Arch.* 68, 191; *Pharm. Viertelj.* 1, 278). When 7 pts. tannic acid are triturated with 1 pt. *iodine* and 300 pts. water, a turbid liquid is produced, which does not give any indication of the presence of iodine when tested with starch; it deposits black-brown crystals free from iodine, amounting to  $\frac{1}{4}$ th of the tannic acid used, and resembling tannic acid in their behaviour to gelatin-solution and alkaloids. The iodated solution is red-brown, strongly acid; does not colour the skin; gives a black precipitate with solution of gelatin, albumin and alkaloids. It dissolves a quantity of iodine equal in weight to the tannic acid employed. On mixing it with lime, tannic acid is precipitated, the whole or nearly the whole of the iodine remaining in solution as iodide of calcium. Sugar of lead added to the solution, throws down iodide, and then tannate of lead. The solution does not yield either iodine or hydriodic acid by distillation, and when evaporated, gives off only a small quantity of iodine-vapour as the mass becomes dry; neither can iodine be detected by starch in the residue of the distillation. (Socquet & Guillermond.)—6. Aqueous *iodic acid* eliminates from tannic acid, even in the cold, carbonic acid mixed with a small quantity of carbonic oxide. (Millon, *Compt. rend.* 19, 272.) *Iodate of potash* produces a dark, and on heating, a nearly black coloration; alcohol does not produce any precipitate in the mixture. (Simon, *Repert.* 65, 205.)—7. *Bromine* acts violently on tannate of potash, and forms a brown resin. (Cahours, *N. Ann. Chim. Phys.* 19, 507.)—8. By small quantities of *chlorine*, aqueous tannic acid is clouded, coloured brown, and altered as by evaporation in contact with the air; a larger quantity of chlorine decomposes it completely (Berzelius).—*Chlorate of potash* scarcely exerts any action upon it (Simon).

9. *Oil of vitriol* dissolves gallo-tannic acid with lemon-yellow or brown-yellow colour, becomes purple-red, and gives off sulphurous acid when moderately heated, and at a stronger heat, becomes pitch-black and forms humic acid (Wackenroder).—By boiling, or by continued digestion at a moderate heat with *dilute sulphuric acid*, tannic acid is resolved into gallic acid (Liebig) and dextro-glucose (Strecker, see page 344). Small quantities of ellagic acid and humous substances are likewise formed, probably as secondary products. (Strecker.) Acetic acid is not produced in this reaction (Liebig).

Liebig and Stas long ago supposed (*Ann. Pharm.* 30, 205) that a carbo-hydrate is formed in this decomposition, in addition to gallic acid.—100 pts. tannic acid yield 22 pts. glucose (Strecker), at most 87.4 pts. gallic acid (Wetherill), as much as 95 pts. gallic acid, together with other products of decomposition, the weight of all these products taken together being equal to that of the tannic acid employed (Knop).

By the use of properly diluted sulphuric (or hydrochloric) acid, nearly the whole of the tannic acid may be obtained in the form of gallic acid (Stenhouse). According to Strecker's equation, 100 pts. tannic acid should yield 82.5 pts. gallic acid and 29.1 pts. glucose (see also the reaction with hydrochloric acid).

The crystallisation of the gallic acid is comparatively rapid and abundant, when gall-nut powder is moistened with dilute sulphuric acid and exposed to sunshine, tufts of crystals then appearing on the surface in a few hours, and additional quantities being obtained by repeatedly moistening the powder with acid and then drying it. Pure tannic acid thus treated likewise yields white crystals of gallic acid (Horsley, *J. pr. Chem.* 72, 192).

Tannic acid boiled with an insufficient quantity of dilute sulphuric (or hydrochloric) acid, forms a nut-brown humous substance, Stenhouse's *melantannic acid*, which is tasteless, reddens litmus, is insoluble in cold, sparingly soluble in hot water, but dissolves in alcohol and in alkalis; the ammoniacal solution forms dark-coloured precipitates with metallic salts (Stenhouse).

When tannic acid is boiled with aqueous *hydrochloric acid* out of contact with the air, ellagic acid and sugar are almost always obtained, their quantities however not bearing any definite proportion to one another (Rochleder & Kawalier). When aqueous tannic acid was precipitated by hydrochloric acid to the amount of one-third, and the solution decanted from the precipitate again precipitated in the same manner to the amount of one-half, the solution decanted from this last precipitate, and treated with hydrochloric acid, deposited the rest of the gallic acid in pure white flocks. On dissolving these in water, and boiling with hydrochloric acid in an atmosphere of carbonic acid, the liquid became yellowish at the boiling heat—but not darker after four hours,—and deposited ellagic acid. The solution left to cool in the atmosphere of carbonic acid, and separated after 24 hours from the ellagic acid, then evaporated down to one-half in vacuo over oil of vitriol and sticks of potash, solidified to crystals of gallic acid, and the other half treated as described at page 340 of this volume, yielded crystals of glucose. In this manner, tannic acid containing 50.69 p. c. carbon, 3.74 hydrogen, and 35.57 oxygen, yielded 5.58 p. c. ellagic acid and 9.49 p. c. sugar  $C^{12}H^{12}O^{12}$ ; but tannic acid with a different amount of carbon, yielded other quantities of the two substances (see page 456). Hence tannic acid, even when freed as completely as possible from admixed ellagic and gallic acid, generally contains a compound which yields ellagic acid,—a second which yields gallic acid (these two acids not being formed one from the other), and perhaps also sugar,—or possibly a third from which the sugar is produced. It is possible indeed, by the method given at page 456, to obtain a tannic acid free from the compound which yields ellagic acid, but not to free it from the second body which yields glucose in the decomposition, although the quantity of sugar may be reduced as low as 4 per cent. The greatest quantity of sugar obtained amounted to 9.49 p. c. of the tannic acid. A tannic acid having the composition found by Strecker, yielded 7.27 p. c. ellagic acid, and 4.96 p. c. sugar (Rochleder & Kawalier). Hence Rochleder & Kawalier regard tannic acid as a glucoside (see also the statements of Knop and Robiquet).

10. *Nitric acid* does not precipitate aqueous tannic acid, or with

difficulty only, but colours it yellow, then red, and decomposes it quickly, with formation of oxalic acid (Stenhouse). — 11. When aqueous tannic acid is mixed with aqueous *osmic acid* of the strength of 3 per cent., an inodorous, deep-blue liquid is formed, transparent only in thin films, and leaving on evaporation a black-blue, amorphous, insoluble layer. On dissolving this residue in aqueous osmic acid, osmic oxide is separated, the reaction being accelerated by heat, and the red-brown filtrate obtained after heating the liquid with ammonia, yields by evaporation brown crystalline needles and a humous substance. The needles contain oxalic acid and an acid very much like suberic acid (Buttlerow, *J. pr. Chem.* 56, 207).

12. Tannic acid boiled with excess of weak *potash-ley* yields gallic acid (Liebig, xii, 398). The solution separated from the gallic acid does not contain acetic acid. By prolonged boiling, the gallic acid is resolved into carbonic and pyrogallic acids (Liebig). In contact with the air it changes, as described at page 401, vol. xii. With cold *potash-ley* in contact with the air, it forms tannoxylic acid (xii: 437, Büchner). Aqueous tannic acid agitated with soda-ley and oxygen, becomes transparent and brownish yellow when supersaturated with dilute sulphuric acid, and yields peroxide of hydrogen to ether (Schönbein, *J. pr. Chem.* 81, 12).

When tannic acid is treated with *alkalis* in a current of hydrogen, gallic acid and a gum  $C^{12}H^{10}O^{11}$  are produced (Rochleder & Kavalier, *Wien. Akad. Ber.* 22, 558). — 13. Tannic acid boiled with *hydrate of baryta*, yields gallic acid and glucate of baryta (Rochleder & Kavalier). Baryta- or lime-water in excess quickly colours tannic acid green, blue, red and yellowish brown; acids decolorise the solution (Wackenroder).

14. When tannic acid is boiled for several hours with an equal weight of *monosulphite of soda* or *potash* and 12 pts. of water, or when the solution is evaporated till it froths up in viscid bladders, a quantity of anhydrous gallic acid is obtained equal to 75—79 p.c., and 5 or 6 per cent. of a second body, which contains an equal number of atoms of carbon, hydrogen and oxygen, but is not sugar (Knop). Knop likewise found small quantities of ellagic acid, which perhaps was previously contained in the tannic acid. On evaporating to complete dryness with sulphite of soda, and redissolving in the smallest possible quantity of boiling water, ellagate of soda remains behind, together with a green fat contained in the tannic acid; after this has been removed by filtration, a quantity of alcohol about equal to 8 or 10 times the weight of the tannic acid used is to be added. By this means a red-brown syrup is precipitated, while sulphite and gallate of ammonia remain dissolved and crystallise from the decanted liquid. The red-brown syrup contains sulphite of soda in combination with a dark brown substance, which acquires a crimson colour with oil of vitriol, and forms a compound with oxalate of soda, which crystallises in needles, but cannot be obtained of constant composition. The syrup dissolves in water and in alcohol, less easily in absolute alcohol, and not at all in ether (Knop, *Chem. Centr.* 1857, 370). — 15. Tannic acid boiled with aqueous *sulphite of ammonia* yields crystalline gallamic acid (xii, 435) and an amorphous substance which remains in the mother-liquor. When the latter is decomposed with bichloride of tin, ammonia (not hydrilamine, xii, 435) and Knop's former *paragallic acid* are obtained, which latter Knop now regards as a mixture of gallic acid with a carbohydrate and water  $C^{14}H^{80}O^{12}$ ,  $C^8H^{80}O^8$ ,  $4H_2O$ .



16. *Chromic acid*, heated with aqueous gallic acid, quickly decomposes it, with evolution of carbonic acid (Hünfeld, *J. pr. Chem.* 16, 361). Bichromate of potash produces a yellow-brown precipitate, which quickly turns black (Wackenroder). — 17. *Peroxide of manganese*, heated with aqueous tannic acid, with or without sulphuric acid, decomposes it, with evolution of carbonic acid and formation of brown extractive matter. No gallic acid is produced in this reaction (Hünfeld). By *permanganate of potash*, aqueous tannic acid is rapidly oxidised, the solution, if concentrated, giving off carbonic acid. In this reaction a body of undetermined constitution is produced, besides carbonic acid and water (Monier). One milligramme of tannic acid dissolved in a litre of water, is sufficient to decolorise the acid solution of the permanganate (Monier). When permanganate of potash is added to a strongly acid solution of tannic acid, the colour of the permanganate disappears quickly at first (the liquid becoming yellow and then colourless), more slowly if a portion of the tannic acid has been decomposed, so that the instant at which the last portion of the tannic acid disappears cannot be recognised with certainty. 100 pts. tannic acid take up about 60 pts. oxygen from the permanganate (Molr, *Titrimethode*, 2 Aufl. Braunsch. 527).

18. Tannic acid reduces *ferric solutions* partially at common temperatures, completely at the boiling heat, to ferrous solutions. (Wackenroder, *vid. inf.*) — 19. From *cupric salts*, it reduces cuprous oxide; from *mercuric chloride*, mercurous chloride; from solutions of *mercurous* or *mercuric oxide*, it gradually throws down metallic mercury. (Wackenroder.) *Carbonate of silver* is reduced by tannic acid, even in the cold. (Schiff, *Ann. Pharm.* 109, 65.)

20. Aqueous tannic acid which remains unaltered when not exposed to the air, decomposes, with evolution of carbonic acid and formation of gallic acid, if it remains in contact with the nitrogenous constituents of the gall-nuts, therefore, in infusion of galls, and more quickly in gall-nuts moistened with water. (Robiquet, Pelouze.) Ellagic acid is formed at the same time. (Erdmann, Mulder.) The formation of mould, which commonly takes place, has no influence on the transformation. (Winckler, *Repert.* 53, 401.) The decomposition takes place even in closed vessels (Nesenbeck, *N. Br. Arch.* 31, 129), and more quickly in proportion as the solution of tannic acid is more dilute. (Robiquet.) The transformation is to be regarded as a fermentation process, inasmuch as it is stopped or retarded by antiseptic substances, as alcohol, wood-vinegar, creosote, mercuric oxide, and corrosive sublimate; moreover gall-nuts freed from tannic acid by ether, excite vinous fermentation in solution of sugar. (Larocque.) The pectase of the gall-nuts is the ferment which excites the gallic acid fermentation, and the simultaneous conversion of the pectose into pectin. The pectase of gall-nuts is also capable of converting the pectin of fruits into pectic acid; and pectase from turnips can excite the gallic acid fermentation. Tannic acid prepared with ether, but not purified, still contains sufficient pectase to give rise to decomposition when dissolved in water. Emulsin, yeast, vegetable, or animal albumin, and legumin, retard, rather than promote, the gallic acid fermentation. (Robiquet.) In the preparation of gallic acid by method 5, page 399, vol. xii, Braconnot observed the formation of alcohol. — Tannate of quinine, which is insoluble in water, is converted by continued digestion with water into soluble gallate of quinine. (Lintner, *N. Repert.* 1, 411; *Pharm. Centr.* 1853, 218.) —

Tannate of soda dissolved in water, together with bicarbonate of soda, and mixed with *yeast*, forms gallic acid and humous substances. (Ranke, *J. pr. Chem.* 56, 161.)

*Combinations.* Tannic acid does not become moist when exposed to the air. (Berzelius.) It is hygroscopic, and cannot be dehydrated by a heat below 120°. (Mulder.) After drying in *vacuo*, it does not lose more than 0·8 p. c. of its weight at 120°, nor any more till it begins to decompose. (Strecker.) The acid dried at the heat of the water-bath, gives off at 150°, 10 p. c. water if it has been obtained from ether, 12·85 p. c. if it has been obtained from water; — the water thus given off is free from empyreumatic odour. (Luboldt.)

Tannic acid dissolves readily in water, forming a colourless frothing liquid.

Sp. gr. of aqueous Tannic acid at 15°, according to Hammer.

Tannic acid per cent.	Sp. gr.	Tannic acid per cent.	Sp. gr.
1 .....	1·0040	6 .....	1·0242
2 .....	1·0080	7 .....	1·0283
3 .....	1·0120	8 .....	1·0325
4 .....	1·0160	9 .....	1·0367
5 .....	1·0210	10 .....	1·0409

¶. Tannic acid is about 200 times less *diffusible* than chloride of sodium: the diffusate contains unaltered tannic acid (Graham, *Chem. Soc. J.* 15, 250). ¶.

Tannic acid is precipitated from its aqueous solution by several salts, as by sal-ammoniac, common salt, sulphate and acetate of potash (not by nitre or Glauber's salts, according to Strecker), by sulphuric and hydrochloric acids (Berzelius), from very concentrated solution by phosphoric, oxalic, and tartaric acids (Wackenroder), and by arsenic acid. (Berzelius.) When boracic acid is dissolved, with aid of heat, in aqueous tannic acid, the mass solidifies on cooling to a white jelly, which dries up to a bulky snow-white mass. (Berzelius.) These precipitates were regarded by Berzelius as compounds of tannic acid with mineral acids; but the precipitate thrown down by sulphuric acid retains, after pressure, only a small and variable quantity of sulphuric acid; that produced by hydrochloric acid gives off all its hydrochloric acid in *vacuo* over quick-lime; hence the precipitates can be regarded only as mixtures of tannic acid with mineral acids, produced because tannic acid is less soluble in acidulated than in pure water. (Strecker.)

Gallo-tannic acid expels carbonic acid from its salts; it precipitates most metallic salts, and unites with the oxides, forming the *gallotannates*. The acid is *terbasic*, its *neutral* (*terbasic* or *ternmetallic*) salts having the formula  $C^{28}H^{10}M^3O^{34}$  (Strecker); but it likewise forms *acid* and *basic* salts. The salts quickly change in contact with the air, and are difficult to obtain pure.

*Tannate of Ammonia.* — Tannic acid absorbs ammonia-gas which is passed over it, forming a compound corresponding to the formula  $C^{28}H^{10}O^{28}, 4NH^3$ , which turns brown at 100° C. giving off water and ammonia. (Mulder.) — By nearly neutralising aqueous tannic acid with ammonia, a yellowish red liquid is obtained, which turns green in contact with the air, and is coloured dark red by excess of ammonia. (Büchner.)

Carbonate of ammonia added to aqueous tannic acid throws down a white precipitate, which changes to a white powder in vacuo. (Berzelius.) An excess of carbonate of ammonia causes the white precipitate produced at first to disappear immediately, and the liquid, after standing for some time, acquires a red-brown colour, and deposits light white flocks. (Büchner.)—Ammonia-gas passed to saturation into a solution of tannic acid in absolute alcohol, throws down white flocks, or if the solution is very strong, a white resin, which becomes friable when repeatedly treated with absolute alcohol. This substance, dried between filtering paper and then over oil of vitriol, forms a resin having a faint brown tint, and very soluble in water. (Büchner.)

				Büchner. mean.	
<i>a.</i>		<i>b.</i>			
108 C	50.35	108 C	51.07	.....	51.08
53 H	4.12	51 H	4.02	.....	4.69
3 N	3.26	3 N	3.31	.....	3.32
68 O	42.27	66 O	41.60	.....	40.91
$2C^{54}H^{22}O^{34}, 3NH^3$ ....		100.00		.....	100.00

*b.* According to Strecker, who regards this compound as the ammonia-salt of an amidated acid of tannic acid.

*Tannate of Potash.* *a. Polybasic?*—The salt *b* forms, with a certain quantity of potash-ley, a yellow solution, which has an astringent but not very alkaline taste, and leaves, when evaporated, a yellow-brown transparent extract soluble in water.—The addition of a larger quantity of potash causes decomposition during the evaporation. (Berzelius.)

*b. Terbasic?*—From a not too dilute aqueous solution of tannic acid, caustic potash, monocarbonate, and bicarbonate of potash, throw down a white powder, which, after washing and pressing, dries up to a white earthy mass, permanent in the air. This substance, dissolved in a small quantity of boiling water, separates on cooling in the form of a white granular mass, which leaves the same earthy substance on being left to dry spontaneously. It dissolves in a larger quantity of water, forming a neutral liquid, which has an astringent taste, and solidifies to a jelly when concentrated. It dissolves in warm aqueous tannic acid, and separates unaltered on cooling. In alcohol it is nearly or quite insoluble. (Berzelius.)

*c. Bibasic.*—Alcoholic potash is added to moderately dilute alcoholic tannic acid till red veins form on the surface.—White crystalline flocks, forming when dry an earthy mass, soluble with greenish colour in water, partly precipitable. The aqueous solution, when evaporated, leaves a brown smeary mass. (Büchner.)

		at 100°.		Büchner. mean.	
54 C	324.0	....	45.48	.....	45.00
22 H	22.0	....	3.09	.....	3.05
34 O	272.0	....	38.18	.....	38.70
2 KO	94.4	....	13.25	.....	13.25
$C^{54}H^{20}K^2O^{34}, 2HO$ .....		712.4	....	100.00	..... 100.00

*Tannate of Soda?*—When aqueous tannic acid, neutralised as nearly as possible with soda-ley, is left to evaporate freely, there remains a greenish grey-yellow semi-crystalline mass, with distinct yellow crystalline laminae on its edges. A small quantity of cold water dissolves a portion of this substance, leaving a salt similar to the potash-salt *b*, which, if dissolved in boiling water, separates as a neutral white powder on cooling. The crystalline salt, which dissolves in cold water, is insoluble in alcohol, and melts therein when heated. It has a slight alkaline reaction, and does not precipitate a solution of gelatin, even after addition of acid. (Berzelius.) A concentrated aqueous solution of tannic acid behaves with caustic soda or its carbonate in the same manner as with potash. When mixed with excess of carbonate of soda, it forms a yellowish solution, which turns green in contact with the air, and deposits a small quantity of yellow-green crystalline precipitate. (Büchner.)

*With 5 at. Base to 2 at. Acid.*—Precipitated by alcoholic soda-ley from a cooled moderately dilute alcoholic solution of tannic acid. From warm or too concentrated solutions, a resin is precipitated. The precipitate, when dried over the water-bath, forms a faintly yellow, earthy, friable mass. With a small quantity of water, it coagulates to a gummy mass, and with a much larger quantity it forms a clear brown solution, which becomes milky as it cools. The concentrated aqueous solution evaporated over oil of vitriol leaves a brown film and laminae. (Büchner.)

	at 100°.			Büchner.
				mean.
108 C .....	648	.....	46.59	..... 46.57
44 H .....	44	.....	3.16	..... 3.26
68 O .....	544	.....	39.11	..... 39.60
5 NaO .....	155	.....	11.14	..... 10.57
<hr/>				
2C <sup>54</sup> H <sup>22</sup> O <sup>34</sup> , 5NaO ....	1391	.....	100.00	..... 100.00

So according to Strecker; Büchner gave the formula 5C<sup>18</sup>H<sup>8</sup>O<sup>12</sup>, 4NaO—HO.

*Tannate of Baryta.*—*a.* Baryta-water added to aqueous tannic acid, throws down a basic salt. (Berzelius.) The precipitate dissolves in aqueous tannic acid, not in excess of baryta-water; it turns green when left to stand, or when washed in contact with the air; also if it has been precipitated with baryta-water, not in excess.

*b.* If carbonate of baryta be added to aqueous tannic acid as long as effervescence takes place, the liquid then filtered, and the filtrate concentrated, only small quantities of flocks separate on cooling; but alcohol added to the brown solution, throws down a white light powder, which, after washing with alcohol, turns brown on drying.

*c.* From warm aqueous solutions of alkaline tannates, chloride of barium throws down a white precipitate, sparingly soluble in cold water, more soluble in boiling water. (Berzelius.) The light flocculent precipitate assumes a very faint reddish colour when washed, and, after drying at 100°, contains 39.7 p. c. C., 2.8 H., 36.8 O., and 20.7 BaO. (Büchner.) Büchner gives the formula 4C<sup>18</sup>H<sup>8</sup>O<sup>12</sup>, 3BaO: Strecker regards the salt as a mixture of terbasic (C<sup>51</sup>H<sup>22</sup>O<sup>34</sup>, 3BaO), and bibasic salt (C<sup>54</sup>H<sup>22</sup>O<sup>34</sup>, 2BaO).

*Strontia* reacts with tannic acid like baryta. (Berzelius.)

*Tannate of Lime.*—Milk of lime, added in excess to aqueous tannic acid, precipitates it completely as insoluble basic salt. (Berzelius.) Chloride of calcium solution does not precipitate aqueous tannic acid (Wackenroder), but from the acid nearly neutralised with ammonia, it throws down the neutral salt, which redissolves during washing. (Berzelius.) The precipitate quickly turns bluish-green, then brown; the white precipitate thrown down from fixed alkaline tannates is almost wholly soluble in water, and dissolves readily in acetic acid. (Wackenroder.)

*Tannate of Magnesia.*—Hydrate of magnesia and *magnesia alba* are coloured yellow by aqueous tannic acid, and throw down nearly all the tannic acid forming a basic compound. (Berzelius, Fr. Müller.)

*Tannate of Alumina.*—Hydrate of alumina, shaken up with aqueous tannic acid quickly unites with it, forming an insoluble compound (Pelouze) which dissolves in excess of tannic acid. (Berzelius.)—*Glucina* and *yttria* react like alumina.

*Tannate of Titanic oxide.*—From hydrochlorate of titanic oxide, neutralised as nearly as possible with ammonia, aqueous tannic acid throws down yellow-red flocks. (Pfaff.)—From acid solutions of titanic acid, infusion of galls throws down at first a brownish precipitate, quickly changing to pale orange-red. (Rose.)

Infusion of galls colours hydrate of *tantallic acid* orange-yellow, and precipitates the *tantallic acid* with the same colour from its acid and alkaline solutions. The light yellow precipitate dissolves in alkalis. (Rose).—The infusion does not alter *alkaline tungstates*, but acids added to the mixture, throw down a thick, chocolate-coloured precipitate.—Tannic acid colours *alkaline molybdates* deep blood-red, and on addition of hydrochloric acid, a blood-red precipitate is formed, which dissolves in a large quantity of water. (Rose.)

With *salts of vanadic oxide*, aqueous tannic acid forms a bluish-inky mixture, which, when left to stand quietly, deposits a black precipitate.—With *alkaline vanadates*, infusion of galls first gives a green, then an inky-black colouring: the mixture diluted with a large quantity of water, forms a clear dark-blue liquid, which gradually turns green in contact with the air. The concentrated mixture may be used as an ink, but changes in contact with the air, the black-blue colour passing into green. The writing is durable, and withstands the action of hydrochloric acid, of chlorine, or of alkalis, but is destroyed by successive treatment with chlorine and alkalis (or by nitric acid: Kr.) (Berzelius).

*Chromic hydrate* forms with aqueous tannic acid an insoluble compound, which is likewise precipitated on mixing chromic salts with tannic acid. (Berzelius.) Infusion of galls does not precipitate chromic salts. (Rose.) *Uranic oxide* behaves with tannic acid like chromic oxide. (Berzelius.) Infusion of galls throws down a red-brown precipitate from neutral uranic salts. (Rose.)—The infusion does not decompose either *arsenites* or *arsenates*. (Rose.)

*Tannate of Antimony.*—Aqueous tannic acid throws down from tartar-emetic a thick white precipitate, which during washing, partly dissolves in the water and is partly carried through the filter, rendering the liquid milky. The white gelatinous, very sparingly soluble

precipitate consists of  $3C^{16}H^8O^{12}, SbO^3$  (Pelouze), or, according to Strecker's formula for tannic acid, of  $C^{24}H^{12}O^{34}, SbO^3, 2HO$ . On the behaviour of tannic acid with tartar-emetie, see Berzelius (*Lehrb.* 3 Aufl. 6, 229).

*Tellurium-salts* are precipitated yellow by infusion of galls.

*Tannate of Bismuth.* Bismuth salts form a yellow precipitate with infusion of galls. 44 pts. of crystallised nitrate of bismuth are decomposed by a slight excess of carbonate of soda, and the washed precipitate is mixed with 20 pts. tannic acid. The compound contains 53 p. c. bismuth-oxide and 47 p. c. tannic acid. (Cap, *Pharm. Viertelj.* 8, 589.)

*Tannate of Zinc* — White precipitate thrown down from zinc-salts by alkaline-salts. (Wackenroder.) — Helm (*N. Br. Arch.* 106, 26; *Pharm. Viertelj.* 11, 99) mixes the solution of 6 oz. sulphate of zinc in 4 lbs. water, with ammonia not in excess, as long as a precipitate is thereby produced; this precipitate is collected, washed, and stirred up with  $3\frac{1}{2}$  oz. tannic acid and water; and the mixture is heated to boiling, drained and dried. Yellowish white powder, insoluble in water.

*Tannate of Cadmium.* — Hot aqueous tannic acid throws down from cadmium-salts a white precipitate, which assumes a yellow-green colour when dry, becomes anhydrous at  $100^\circ$ , and contains 21.4 p. c.  $CdO$ . Insoluble in water and in alcohol. (Schiff.)

*Stannous Tannate.* — Stannous hydrate takes up tannic acid from its aqueous solution; stannous salts are precipitated by tannic acid. (Berzelius.) The white flocks precipitated from aqueous tannic acid, dissolve readily in excess of protochloride of tin; those precipitated from tannate of soda are but very slightly soluble. (Wackenroder.) — *Stannic hydrate* decolorises infusion of galls when digested with it, and appears to take up all the tannic acid. (Proust, Davy.) Infusion of galls precipitates hydrochlorate of stannic oxide. (Wuttig.)

*Tannate of Lead.* — Tannic acid heated with excess of lead-oxide to  $120^\circ$  —  $140^\circ$ , gives off from 4.1 to 4.4 p. c. water (3 at. = 4.4 p. c.) (Strecker). Part of the tannic acid is apt not to enter into combination with the lead oxide, and may be dissolved out of the dried mass by water, another portion is altered by contact with the air. (Strecker.) Mulder obtained in three experiments, from 2.3 to 3.0 p. c. loss of water; in one experiment, 4, and in another, 5.7 per cent. Hydrate of lead abstracts tannic acid from its aqueous solution (Berzelius). Concentrated aqueous tannic acid dissolves rather large quantities of hydrate of lead, which are for the most part precipitated on addition of water. (Ritter.)

By precipitating aqueous tannic acid with neutral acetate of lead, salts may be formed containing quantities of lead-oxide, varying from 34.12 to 64 p. c.; among them are three definite lead-salts, the rest being mixtures of these with each other. (Strecker.) Mulder obtained, under different circumstances, 5 salts which, at  $120^\circ$ , contained  $\frac{3}{2}$ , 2, 3, 4, and 5 at. lead-oxide to 1 at. tannic acid ( $C^{28}H^{10}O^{17}$  according to Mulder). By precipitating tannic acid or tannate of potash with basic acetate of lead, a basic salt is obtained, which becomes yellow-green during washing. (Berzelius.) All the lead-salts are yellow when recently precipitated, excepting the neutral (terbasic) salt. Their organic sub-

stance exhibits at  $120^{\circ}$ , the composition expressed by the formula  $C^{54}H^{19}O^{31}$ ; it does not give off any water, when further exposed to heat, but the salts decompose at  $150^{\circ}$ . They are difficult to wash, and during washing, absorb oxygen from the air, assuming a darker colour from the surface inwards. (Strecker.)

a. *With 9 or 10 at. Lead-oxide.*—When aqueous tannic acid is poured into a boiling aqueous solution of neutral acetate of lead, so that this salt remains in excess, the filtrate further precipitated by tannic acid, and the mixture boiled for a quarter of an hour in contact with a large quantity of free acetic acid, a yellowish powder is obtained, which at  $100^{\circ}$  becomes whitish grey, and contains 20.24 p. c. C., 1.11 H., and 63.0 to 64.09 p. c. PbO. (Liebig, *Ann. Pharm.* 26, 128). This, according to Strecker, is the salt  $C^{54}H^{19}Pb^3O^{34}$ , 6PbO (calc. 20.23 p. c. C., 1.19 H., 13.50 O., and 63.06 PbO).—The precipitate thrown down from excess of boiling sugar of lead by dilute aqueous tannic acid, when collected after a few minutes' boiling, and dried in vacuo, gave off at  $120^{\circ}$ , 1.54 p. c. water (3 at. water = 1.5 p. c.) and then contained 64.7 p. c. lead-oxide, corresponding to the formula  $C^{54}H^{19}Pb^3O^{34}$ , 7PbO. When dried it slowly absorbs carbonic acid from the air. (Strecker.)

	<i>In vacuo.</i>			Strecker.	
54 C .....	324	.....	18.64	.....	18.2
22 H .....	22	.....	1.26	.....	1.0
34 O .....	272	.....	15.65	.....	17.1
10 PbO .....	1120	.....	64.45	.....	63.7
<hr/>					
$C^{54}H^{19}Pb^3O^{34}$ , 7PbO + 3aq. ....	1738	.....	100.00	.....	100.0

b. *With 6 at. Lead-oxide.*—Luke-warm aqueous tannic acid is precipitated by excess of neutral acetate of lead, and the precipitate is washed with boiling water. After drying in vacuo, it sustains, at  $120^{\circ}$ , a loss of weight amounting to 2.2 per cent. (3 at. water = 2.1 p. c. Strecker).

	<i>In vacuo.</i>			Strecker. <i>mean.</i>	
54 C .....	324	.....	25.11	.....	24.85
22 H .....	22	.....	1.71	.....	1.40
34 O .....	272	.....	21.09	.....	20.95
6 PbO .....	672	.....	52.09	.....	52.80
<hr/>					
$C^{54}H^{19}Pb^3O^{34}$ , 3PbO + 3aq. ....	1290	.....	100.00	.....	100.00

c. *With 3 at. Lead-oxide.*—When aqueous tannic acid is precipitated by sugar of lead, a white precipitate is formed, which assumes a darker colour when exposed to the air. This precipitate treated with boiling water, gives up tannic acid, and leaves neutral tannate of lead, which becomes gummy and darker coloured in contact with ammonia, without altering its amount of oxide of lead (34.21 p. c.). After deduction of the oxide of lead, it contains 51.50 p. c. C., 3.79 H., and 44.71 O. (Berzelius) and consists, according to Strecker, of  $C^{54}H^{19}Pb^3O^{34}$  + 4H<sub>2</sub>O. The precipitate thrown down by neutral acetate or nitrate of lead from excess of aqueous tannic acid, contains at  $120^{\circ}$ , 32.86 p. c. C., 2.81 H., and 33.79 to 34.27 PbO (Pelouze). Strecker gives the formula  $C^{54}H^{19}Pb^3O^{34}$  + 5 H<sub>2</sub>O, which requires 33.33 p. c. C., 2.47 H., 34.57 PbO, and 29.63 O.—The terbasic salt may be prepared by adding a

dilute solution of neutral acetate of lead to aqueous tannic acid, either in the cold, or between  $40^{\circ}$  and  $50^{\circ}$ , in such quantity, that part of the tannic acid may remain in solution. After drying in vacuo, it gives off 2.8 p. c. water at  $120^{\circ}$  (3 at. = 2.83 p. c.) (Strecker.)

	at $120^{\circ}$ .		Strecker.	
54 C.....	324	.....	34.95	..... 33.7
19 H .....	19	.....	2.06	..... 1.9
31 O .....	248	.....	26.75	..... 28.2
3 PbO .....	336	.....	36.24	..... 36.2
<hr/>				
$C^{54}H^{19}Pb^3O^{34}$ .....	927	.....	100.00	..... 100.0

From *ferrous salts* aqueous tannic acid throws down—but only from very concentrated solutions—a white gelatinous precipitate which dissolves on addition of water. (Berzelius.)

*Ferric Tannate.* Ferric salts yield, with very dilute aqueous tannic acid, a dark-blue transparent liquid, which after a while becomes dark green, and deposits green flocks; at still greater degrees of dilution, the mixture immediately assumes a dark green colour, without yielding any precipitate. (Berzelius.)—The blue-black colouring passes quickly into brownish-green, then into olive-green, and finally into greenish-brown, the liquid becoming clear in a shorter time in proportion as the iron-salt is in greater excess; with ferric-acetate, however, the iron-black colour is permanent. (Pfaff.) The blue-black colouring of ferric salts is changed by the stronger acids, especially by tartaric acid, to green; by alkalis, to red (Geiger); if, however, the liquid altered by acids be set aside for 24 hours, then decanted from the precipitate, and the latter treated with pure water, the liquid again becomes black; hence it appears that the green colouring arises from the mixture of the yellow ferric tartrate with the ferric tannate. (Berzelius, *Mag. Pharm.* 31, 362.)—Ferric salts are partially reduced as soon as they are mixed with tannic acid, and at the boiling heat the reduction is complete. (Wackenroder.)

When aqueous tannic acid is precipitated by pouring ferric sulphate into it, the precipitate, after washing and drying at  $122^{\circ}$ , contains 12.02 p. c. ferric oxide. (Pclouze.) Strecker gives the formula  $C^{54}H^{19}O^{31}, Fe^2O^3$  (calc. 11.92  $Fe^2O^3$ ). Wittstein found the quantity of ferric oxide in the precipitate very variable; the only way in which he could obtain a constant compound was by precipitating ferrous sulphate with aqueous tannic acid and exposing the precipitate to the air.

a. When a solution of 2 at. ferrous sulphate is mixed with 1 at. aqueous tannic acid, and the mixture is exposed to the air for six weeks or longer, and frequently stirred, the dark indigo-blue precipitate washed, and dried at  $100^{\circ}$ , contains 8.4 p. c.  $Fe^2O^3$ , a small portion of the iron being, however, in the state of protoxide. The filtered liquid again exposed to the air yields a further precipitate, containing an equal proportion of ferric oxide. The filtrate does not contain gallic acid. (Wittstein.)

b. When ferric sulphate is added to aqueous tannic acid, in such quantity, that the filtrate is still clouded by an iron-salt, the resulting dark-blue precipitate contains very little ferrous oxide, and yields on ignition 14.90 p. c.  $Fe^2O^3$ . When, on the other hand, tannic acid is added



to ferric sulphate, as long as a precipitate is formed, the precipitate yields 15.4 p. c.  $\text{Fe}^2\text{O}^3$ . The black-green filtrate contains ferrous oxide, the quantity of which increases on boiling, but it is only when more tannic acid is added that the whole of the sesquioxide of iron is reduced to protoxide. (Wittstein.)

c. When 1 at. ferric acetate is added to 1 at. aqueous tannic acid ( $\text{C}^{54}$ ), the resulting black-blue precipitate, after being washed with cold water and dried at  $100^\circ$ , contains 18.75 p. c. ferric oxide, together with a small quantity of free tannic acid, and after this has been dissolved out by ether, 100 pts. of the precipitate yield 20.15 p. c. ferric oxide. The precipitate likewise contains a small quantity of ferrous oxide. — The filtrate from c leaves, on evaporation, a dark-blue, resinous, very astringent residue, which dissolves completely with dark-blue colour in water and alcohol. — This residue treated with ether, yields tannic acid, whereby it loses almost entirely its solubility in water and in alcohol, becomes nearly black, and when dried at  $100^\circ$ , contains 13.4 p. c. ferric oxide. (Wittstein.)

d. When aqueous tannic acid is dropped into a very dilute solution of ferric acetate as long as it produces any precipitate, the liquid loses its yellow-red colour, and becomes colourless, the precipitate is rather brown than blue, black after drying, and yields, when dried at  $100^\circ$ , quantities of ferric oxide, varying from 42.85 to 56.25 p. c., part of it being, however, present as ferrous oxide. A colourless filtrate is likewise obtained, when, on the other hand, ferric acetate is added to tannic acid, as long as any precipitate is formed. The precipitate yields 25 p. c.  $\text{Fe}^2\text{O}^3$ ,  $\frac{1}{8}$  of which is present as protoxide. (Wittstein.)

On ferric tannate, see further Winckler (*Repert.* 95, 77); Collomb (*Rev. scient.* 16, 477); Wackenroder (*N. Br. Arch.* 27, 269); Geiseler (*N. Br. Arch.* 89, 165).

*Cobalt-salts* are precipitated yellowish white by infusion of galls; *nickel-salts* greenish-white.

*Cupric Tannate.* — Cupric hydrate abstracts tannic acid from its aqueous solution. (Berzelius.) — The salt is obtained by double decomposition in grey-brown flocks, which are reddish-white or brownish-grey, according as the tannic acid or the copper-salt is in excess. It is dissolved by potash, with separation of cuprous oxide; completely by ammonia, only when the tannic acid is in excess; the latter solution is not altered by hydrosulphuric acid. (Wackenroder.)

*Mercurous Tannate.* Mercurous oxide abstracts tannic acid from its aqueous solution; mercurous salts are precipitated by tannic acid (Berzelius). From mercurous nitrate, tannate of potash precipitates a powder which is nearly white at first (yellow, soon turning green, according to Wackenroder), which darkens on standing, appears yellow-green when dry, and contains 44.96 p. c.  $\text{Hg}^2\text{O}$ . It is not soluble either in hot or in cold water, even after addition of tannic acid. Aqueous ammonia converts it into black ammonio-mercurous tannate containing 76.78 p. c.  $\text{Hg}^2\text{O}$ . (Harff.)

*Mercuric Tannate.* — Tannic acid is precipitated from its aqueous solution by mercuric oxide. It precipitates mercuric salts, excepting the chloride (Berzelius). From mercuric nitrate it throws down a thick, brick-red precipitate, which is insoluble in excess of the pre-

precipitant, and on standing acquires a dirty yellow colour, and is found to contain mercurous oxide (Wackenroder). The precipitate thrown down from mercurous nitrate by tannate of potash is light yellow at first, but becomes darker after a while, yellow-brown on drying, and contains 32.13 p. c.  $\text{HgO}$ . Caustic ammonia poured upon it converts it into dark brown, nearly tasteless ammonio-mercuric tannate, containing 64.64 p. c.  $\text{HgO}$ . (Harff, *N. Br. Arch.* 5, 294.)

*Oxide and nitrate of silver* form black-brown precipitates with aqueous tannic acid (Berzelius, Fr. Müller).—From *bichloride of platinum*, infusion of galls throws down pale yellow flocks (Pfaff).

Tannic acid dissolves in *hydrated*, more abundantly than in *absolute alcohol* (Pelouze).—According to Pelouze, Bolley and Luboldt, it dissolves but sparingly in *anhydrous ether*, and, according to Strecker and others, remains perfectly pulverulent when covered with it, while, according to Mohr, it dissolves in considerable quantity. With *ether containing water*, it forms, after some seconds, a very heavy liquid, like that which separates in the preparation of tannic acid, as described at page 453 of this volume. Of the two layers thus formed, the lower consists of tannic acid, which has taken up the water of the ether, and only a very small quantity of ether, while the upper layer contains ether, a small quantity of tannic acid, and the foreign substances taken up with it (Pelouze). When tannic acid dried at  $110^{\circ}$ , is covered with anhydrous ether, the solution standing above the excess of pulverised tannic acid, after being agitated for a considerable time, contains in solution only 0.206 p. c. at  $5^{\circ}$ , and 0.384 p. c. at ordinary temperatures. On adding to the ether half a volume per cent. of water, the tannic acid, which has hitherto been greyish-yellow and pulverulent, deliquesces to brownish lumps, and on addition of a few drops more water, to a syrup. After addition of 1 volume per cent. of water, the supernatant ether contains 1.2 p. c. tannic acid in solution. On continuously dropping water into the mixture and agitating, three layers are formed, the lowest of which is syrupy, and contains 0.297 grm. tannic acid in a cubic centimetre. The middle layer is somewhat lighter than the lowest, and contains in a cubic centimetre 0.082 grm. tannic acid dissolved in a large quantity of water and a small quantity of ether. The syrupy layer contains both ether and water, and is perhaps a tannate of ether and water, analogous to sulphovinic acid (Bolley, *Chem. Soc. Q. J.* 13, 295; *Ann. Pharm.* 115. 63).

Tannic acid (crude) dried at  $150^{\circ}$  remains pulverulent when covered with 10 pts. of anhydrous ether, while the supernatant ether takes up 2 or 3 p. c. of solid constituents, chiefly the foreign substances mixed with the tannic acid. Water, either present in the tannic acid or the ether, or subsequently added, is greedily absorbed by the tannic acid, and causes it to deliquesce to a viscid mass or a syrup, which does not mix with the excess of ether. When a solution of 100 pts. tannic acid in 100 pts. water is mixed with 150 pts. ether, the liquid, if agitated and left at rest at a temperature of  $18^{\circ}$ , separates into three layers, the lowest of which has a sp. gr. of 1.07, takes up half the total space, and contains 40.5 p. c. tannic acid, 42.2 ether, and 17.3 water. The middle layer, which has a density of 1.02, contains 14.15 p. c. tannic acid, 10.09 ether, and 75.76 water; the uppermost, of density 0.752, is chiefly ether, containing in solution small quantities of foreign matters and water. Also, when 20 grms. tannic acid, 39 grms. ether

and 20 grms. water are shaken up together and then left at rest, three layers are formed, the lowest of which increases by continual agitation at  $14.5^{\circ}$ , at the expense of the upper, till it occupies 36.5 and the upper 17.5 pts. of the entire space, the middle layer, which remains unaltered, occupying 20 pts. The bottom layer, when removed with the pipette, is found to be soluble in 4.5 to 5.5 pts. of water, more abundantly in lukewarm than in cold water. But if water be added to the mixture as it stands, divided into three layers, a quantity equal to 11 times the volume of the bottom layer will be required to dissolve it (the top layer at the same time diminishing to  $\frac{3}{5}$ ) because the water dissolves the bottom layer only so far as it can take up ether. Water saturated with ether dissolves only  $\frac{1}{2}$  of the bottom layer. The bottom layer is therefore hydrated *tannic acid* containing ether in solution; the middle layer is *water* containing ether and tannic acid; and the top layer is *ether* which has taken up water, tannic acid, and the foreign constituents (Luboldt, *J. pr. Chem.* 77, 357). According to Mohr, on the contrary (*Ann. Pharm.* 61, 352), the lowest of the three layers contains tannic acid dissolved in water; the middle layer, tannic acid dissolved in ether. This statement, and another made by Mohr, to the effect that tannic acid deliquesces to a syrup in anhydrous ether, and that by addition of more tannic acid, the ether may be completely converted into this syrup, are not reconcilable with the experiments above described. (See also Guibourt & Robiquet *loc. cit.*; Sandrock, *N. Dr. Arch.* 72, 265.)

The viscid syrup which separates at the bottom of the mixture of tannic acid, water, and ether, unites with the supernatant ether on addition of alcohol to a thin filterable liquid (Mohr).

Tannic acid dissolves in *acetone*, with evolution of heat, the solution drying up to a jelly and leaving a powder which has the aspect of tannic acid (Knop).

*Tannic Acid with Acetone and Ammonia.* — Tannic acid is dissolved in 4 or 5 pts. acetone, the solution is heated to the boiling point, and aqueous ammonia is added, with agitation, till the liquid smells strongly of it. Two layers are then formed, the lower of which is to be repeatedly stirred up with absolute alcohol (whereupon it becomes pasty, and ultimately solid and friable), collected on a filter, pressed, and placed over oil of vitriol, before it can take up water from the air. The mass, which becomes brittle in 24 hours, is triturated and dried for a month over chloride of calcium. White or brownish powder having the taste and the other characters of tannic acid. Soluble in water, not in absolute alcohol. Contains from 49.2 to 50.15 p. c. carbon, 4.7 to 5.5 hydrogen, and 2.8 to 3.5 nitrogen, whence Knop calculates the formula  $C^{42}H^{25}NO^{55} = 2C^{18}H^9O^{12} + C^6H^6O^2 + NH^3$  (Knop, *Chem. Centr.* 1860, 278; abstr. *Rép. Chim. pure*, 2, 372). Till the presence of acetone in this compound has been actually demonstrated, we may be allowed to regard it as tannate of ammonia (p. 463). Kr.

Tannic acid does not unite with *urea*. (Hlasiwetz *Wien. Akad. Ber.* 20, 208). — It does not dissolve in *picamar* (p. 162) even at the boiling heat (Reichenbach, *Schw.* 68, 355). — It dissolves in 6 pts. *glycerin* (Cap & Garot, *N. J. Pharm.* 26, 81; *Pharm. Viertelj.* 4, 271); in *bitter-almond oil* in almost all proportions, the solution, which turns brown in contact with the air, slowly depositing crystals of benzoic acid (Knop). It dissolves in other oils, both fixed and volatile.

Tannic acid precipitates the *alkaloids* from their saline solutions (see vii, 185). It precipitates *starch-solution* and *albumin*. — From solution of *gelatin*, it throws down a white precipitate, which dissolves in excess of the gelatin, especially when heated; if obtained with excess of tannic acid, it presents the aspect of a grey, highly elastic, not perfectly soluble skin. Addition of a large quantity of common salt makes the tannate of gelatin quite (Wackenroder) or nearly insoluble (Fr. Müller). Tannic acid unites with animal *skin* [but not in atomic proportion (Knop, *Dingl.* 149, 305 and 378)], forming tanned leather.

### Appendix to Gallo-tannic Acid.

#### A.—Morintannic Acid and Morin.

#### Morintannic Acid.



R. WAGNER (1850). *J. pr. Chem.* 51, 82; abstr. *Pharm. Centr.* 1851, 33; *Ann. Pharm.* 76, 349. — *J. pr. Chem.* 52, 449; abstr. *Ann. Pharm.* 80, 315; *Pharm. Centr.* 1851, 385 and 406; *N. J. Pharm.* 22, 66; *Compt. chim.* 1851, 104.

Different from the *Moringic acid* of Walter (*Compt. rend.* 22, 1143). According to Delfs (*N. J. Pharm.* 14, 166; *Kopp's Jahresber.* 1860, 278), morintannic acid is a mixture of a yellow uncrystallisable tannin with morin, and may be converted into colourless morin by recrystallisation from water.

*Occurrence.* In the yellow wood of *Mactura tinctoria* (*Handb.* viii, *Zoochem.* 76.) The deposit in the middle of the blocks consists chiefly of this acid.

*Formation.* Ruffinoric acid is converted into morintannic acid by boiling with aqueous alkalis.

*Preparation.* The block is split lengthwise, and the dirty yellow, here and there flesh-coloured lumps, having a red-brown crystalline fracture, which are deposited in the middle of it, are separated with a chisel. They are purified by repeated crystallisation from boiling water, and then dissolved in a larger quantity of boiling water acidulated with hydrochloric acid. The solution, which becomes turbid on cooling, in consequence of the separation of a reddish resin, is repeatedly filtered till it remains clear, then left to itself, the acid slowly separating in the form of a light yellow crystalline powder.

*Properties.* Light yellow powder consisting of microscopic, pale yellow, transparent needles. Has a sweetish astringent taste, like the inner bark of the walnut. Reddens litmus.

at 100°.				Wagner.
				mean.
18 C .....	108 .....	55.10 .....		55.17
8 H .....	8 .....	4.08 .....		4.41
10 O .....	80 .....	40.82 .....		40.42
<hr/>				
$\text{C}^{18}\text{H}^8\text{O}^{10}$ ....	196 .....	100.00 .....		100.00

Isomeric with morin. — Gerhardt (*Traité*, 3, 889) regards the formulæ  $C^{28}H^{12}O^{16}$  and  $C^{58}H^{26}O^{30}$  as likewise possible. Hlasiwetz (*Ann. Pharm.* 107, 247) suggests the formula  $C^{14}H^6O^8$ , regarding morintannic acid as probably homologous with lecanoric acid (xii, 577) and evernic acid. Hlasiwetz's formula would explain the resolution of morintannic acid into carbonic acid and pyrocatechin,  $C^{14}H^6O^8 = 2CO^2 + C^{12}H^6O^4$ . — Respecting the formula of morintannic acid, see also Laurent (*Compt. rend.* 35, 161) and Wagner's reply (*J. pr. Chem.* 57, 441), also Strecker (*Ann. Pharm.* 90, 372).

*Decompositions.* 1. The acid dried at  $100^\circ$ , melts in the metal-bath at  $200^\circ$ , gives off at  $250^\circ$ , a strongly acid water, and is converted into a brown-black liquid, which decomposes completely between  $270^\circ$  and  $300^\circ$ , evolving a large quantity of carbonic acid, and yielding a brown distillate, consisting of carbolic acid and pyrocatechin (xi, 379) the latter solidifying in the crystalline form on cooling. Wagner at first doubted the identity of the crystals with pyrocatechin, but Eissfeldt (*Ann. Pharm.* 92, 106) confirmed it. — Morintannic acid distilled with excess of lime yields a liquid soluble in water, and containing pyrocatechin. — 2. When aqueous morintannic acid is left for three months in a closed vessel exposed to the sun, the smell and taste of carbolic acid are developed, and the liquid yields that acid when distilled. — 3. Morintannic acid triturated with oil of vitriol forms a brown-yellow solution, which after standing for some time, deposits brick-red rustannic acid, and when heated, gives off sulphurous acid with a strong odour of carbolic acid. No sugar is formed in this reaction, or only a trace after very long boiling with dilute sulphuric acid. (Wagner, *J. pr. Chem.* 57, 442, and 61, 504.) — 4. Chlorine passed into aqueous morintannic acid forms a brown resin. — 5. Morintannic acid, boiled for some time with strong hydrochloric acid, emits the odour of carbolic acid, and decomposes completely, with separation of mould. On boiling it with dilute hydrochloric acid, a red solution is formed, which, after a few days, deposits rufimoric acid. — 6. With boiling dilute nitric acid, it forms a brown resin soluble in hot alcohol, together with oxalic acid. The red-brown solution in strong nitric acid yields, on evaporation, pale yellow plates of styphnic acid (xi, 228). — 7. The dark yellow solution of morintannic acid in caustic or carbonated alkalis soon turns brown, and afterwards brown-black when exposed to the air. — 8. The acid detonates violently when triturated with chlorate of potash. — 9. When triturated with peroxide of manganese and sulphuric acid, it rapidly gives off carbonic acid, and is completely decomposed, with production of formic acid. — 10. When aqueous morintannic acid is boiled with peroxide of lead, the latter assumes a reddish yellow colour, the liquid becomes decolorised, and retains only a trace of lead in solution, and the resulting insoluble lead-salt, decomposed by hydrosulphuric acid, yields a humous acid. The acid triturated with dry peroxide of lead, takes fire, emits sparks, and gives off a pungent odour. — 11. It is completely destroyed by chromic acid, giving off the odour of carbolic acid, and forms a red-brown precipitate when heated with aqueous bichromate of potash. — 12. Heated with aqueous cupric acetate, it deposits cuprous oxide; it reduces mercuric chloride to mercurous oxide, after heating with potash; carbonate of silver even in the cold; nitrate of silver, after boiling with ammonia; terchloride of gold in the cold. — 13. Boiled with ferrocyanide of potassium, it eliminates prussic acid, and deposits yellow-brown flocks. When boiled for some time with ferricyanide of potassium, it gives off a large quantity of prussic acid, and separates prussian blue.

*Combinations.* Morintannic acid dissolves in 6·4 pts. water at 20°, and in 2·14 pts. boiling water, forming a yellow solution.—The aqueous acid is not altered by *phosphoric, sulphuric, hydrochloric, or arsenic acid*, being thereby distinguished from gallotannic acid. The solution of the acid in boiling water, mixed with *boracic acid*, yields, on cooling, a jelly made up of extremely fine laminae.

Morintannic expels carbonic acid from *alkaline and earthy carbonates* at the boiling heat, but not in the cold; also prussic acid from *cyanide of potassium*. It dissolves with deep yellow colour in *caustic alkalis* and *alkaline carbonates*.

*Morintannate of Lime.*—Aqueous morintannic acid is boiled with carbonate of lime, as long as carbonic acid continues to escape; the liquid is filtered at the boiling heat; the yellow-brown flocks which separate after some hours, are collected on a filter and dissolved in alcohol; and the filtered solution is precipitated by pouring it into ten times its volume of water. The yellow microscopic crystals which then fall to the bottom, contain, after pressing and drying at 100°, 7·7 p. c. lime, and after one recrystallisation, 7·18 p. c. ( $\text{CaO}, 2\text{C}^{18}\text{H}^6\text{O}^8 + \text{HO} = 7·12 \text{ p. c. CaO.}$ )—This salt exactly resembles the lime-compound of morin (p. 479) in appearance, and in its behaviour when heated and towards solvents, but it is precipitated blackish green by aqueous ferric chloride, whereas the lime-compound of morin is reddened thereby.

Morintannic acid precipitates *tartar-emetic* yellow-brown; *protochloride of tin* reddish yellow.

*Morintannate of Lead.*—a. *Bibasic?*—When a boiling aqueous solution of morintannic acid is precipitated by basic acetate of lead, the chrome-yellow, non-crystalline precipitate contains, after washing and drying, from 56·9 to 57·5 p. c. lead-oxide ( $2\text{PbO}, \text{C}^{18}\text{H}^6\text{O}^8 = 55·5 \text{ p. c. PbO.}$ )

b. 4 at. Base to 3 at. Acid?—1. The aqueous acid is precipitated by neutral acetate of lead; the chrome-yellow precipitate is dissolved in boiling water; and the lemon-yellow crystalline powder which precipitates on cooling, is collected. The filtered mother-liquor, when left to stand for some time, deposits flocks of variable composition, which constitute the sole product, if the boiling has been too long continued.—2. When hydrate of lead is boiled with the aqueous acid, and filtered hot, crystals are likewise obtained, and the mother-liquor turns brown from partial decomposition. The salt is likewise coloured dark-brown by dilute nitric acid.

at 100°.				Wagner.
54 C .....	324 .....	32·17 .....	32·01	
21 H .....	21 .....	2·08 .....	2·17	
27 O .....	216 .....	21·45 .....	21·55	
4 PbO .....	446 .....	44·30 .....	44·27	
<hr/>				
3C <sup>18</sup> H <sup>7</sup> O <sup>9</sup> , 4PbO .....	1007 .....	100·00 .....	100·00	

Gerhardt (*Traité*, 3, 891) resolves this formula into  $3\text{C}^{36}\text{H}^{12}\text{Pb}^2\text{O}^{18} + 2(\text{PbO}, \text{HO}) + 4\text{aq.}$

Aqueous morintannic acid forms a green-black precipitate with *ferrous sulphate*, soluble with yellow-brown colour in acetic acid. From excess of *ferric hydrochlorate* it throws down a black-green precipitate, which, after washing and drying at 100°, contains 13·2 p. c. ferric oxide ( $\text{Fe}_2\text{O}_3, 3\text{C}^{18}\text{H}^5\text{O}_7 = 13\cdot8$  p. c.  $\text{Fe}_2\text{O}_3$ ). It forms a yellow-brown precipitate, with *protochloride of tin*, and throws down yellow flocks after a while from the *bichloride*.

It dissolves easily in *wood-spirit*, *alcohol*, and *ether*. The concentrated ethereal solution is greenish by reflected, yellow-brown by transmitted light. — It is insoluble in *rock-oil*, *oil of turpentine* and *fixed oils*. — It is completely precipitated by *solution of gelatin* (Wagner).

### Rufimoric Acid.



WAGNER. *J. pr. Chem.* 52, 462.

*Formation.* When morintannic acid is dissolved in oil of vitriol or boiled with hydrochloric acid. The reaction is not attended with the evolution of any gas except traces of sulphurous acid.

*Proportion.* 1. Pulverised morintannic acid is triturated with oil of vitriol; the brick-red mass which separates after standing for some time is collected, washed with cold water till the water scarcely reddens litmus, then dissolved in the smallest possible quantity of boiling alcohol; the greater part of the alcohol is removed from the filtrate by evaporation; and the rufimoric acid is precipitated by pouring the liquid into 50 times its volume of cold water. The bulky red flocks are washed on the filter with cold water, pressed between paper, and dried without warming. When the quantity of material is somewhat considerable, the precipitate coagulates into a viscid mass, which is apt to enclose sulphuric acid; hence it is better to operate with small quantities. — 2. The red solution obtained by digesting morintannic acid with oil of vitriol is diluted with water, exactly neutralised with carbonate of soda, and acidulated with a few drops of acetic acid; the boiling solution is precipitated with acetate of copper; and the red-brown precipitate is decomposed under water with hydrosulphuric acid. The greater part of the rufimoric acid then remains, mixed with the sulphide of copper, and may be extracted by boiling alcohol and obtained in the solid state by evaporating the alcoholic solution.

*Properties.* Dark red mass, yielding a powder of a fine red colour. The solution has an acid reaction.

at 100°.				Wagner.
				mean.
14 C .....	84 .....	54·19 .....	54·29 .....	
7 H .....	7 .....	4·52 .....	4·54 .....	
8 O .....	64 .....	41·29 .....	41·17 .....	
<hr/>				
$\text{C}^{14}\text{H}^7\text{O}^8$ .....	155 .....	100·00 .....	100·00 .....	

Perhaps identical with carminic acid. (Wagner.)

*Decompositions.* 1. Rufimoric acid is not altered at  $130^{\circ}$ , but when more strongly heated, it gives off vapours which partly condense to colourless crystals of pyrocatechin (xi, 379). — 2. Chlorine-water converts it into brown flocks. — 3. With hot nitric acid, it forms a yellow solution containing oxalic acid, and an acid different from picric acid. — 4. The dark red solution in potash-ley or baryta-water becomes dark yellow when boiled, the rufimoric acid being then converted into morintannic acid and the products of its decomposition by alkalis.

*Combinations.* Rufimoric acid is but slightly soluble in pure water, but in presence of the smallest quantity of ammonia it dissolves in all proportions. — With oil of vitriol it forms a red solution, only partially precipitable by water. — It dissolves in hydrochloric acid.

Rufimoric acid dissolves in alkalis and alkaline carbonates, forming a wine-red solution, which exhibits a tinge of yellow if morintannic acid is also present. The carmine-coloured solutions are but very slowly decolorised in contact with the air. Alcoholic potash, added to alcoholic rufimoric acid, throws down a dark red, viscid precipitate. — With chloride of barium, alum, or protochloride of tin (after addition of ammonia), it forms dark-red lakes.

*Rufimorate of Lead.* — The acid forms a dark red precipitate with neutral acetate of lead, cherry-red with nitrate of lead. The salt is prepared by precipitating the alcoholic solution of the acid with alcoholic acetate of lead, washing the precipitate with alcohol, and drying it at  $100^{\circ}$ . Dark scarlet powder, insoluble in water and alcohol, but soluble with yellow-red colour in acetic acid, with carmine-colour in potash-ley. Contains from 59.1 to 59.4 p. c.  $\text{PbO}$ ., and is therefore perhaps  $2\text{PbO}, \text{C}^{14}\text{H}^7\text{O}^8$  (calc. 59.1 p. c.  $\text{PbO}$ ).

Rufimoric acid colours ferric hydrochlorate green, without forming a precipitate.

*Rufimorate of Copper.* — The acid throws down from cupric acetate, brown-red flocks, which, after washing and drying at  $100^{\circ}$ , contain, on the average, 27.7 p. c. cupric oxide, and are therefore  $3\text{CuO}, 2\text{C}^{14}\text{H}^7\text{O}^8$  (calc. 27.75 p. c.  $\text{CuO}$ ).

Rufimoric acid forms a brown-red precipitate with mercurous nitrate, reddish with mercuric oxide. It does not precipitate nitrate of silver.

It dissolves readily in alcohol, sparingly in ether.

## Morin.



CHEVREUL. (1830). *J. Chim. méd.* 6, 158. — *Chimie appliquée à la teinture*, 2, 150.

R. WAGNER. *J. pr. Chem.* 51, 82; abstr. *Pharm. Centr.* 1851, 33; *Ann. Pharm.* 76, 347; *Chem. Gaz.* 1851, 21; *N. J. Pharm.* 19, 149. — *J. pr. Chem.* 52, 449; abstr. *Ann. Pharm.* 80, 315; *Pharm. Centr.* 1851, 385 and 406; *N. J. Pharm.* 22, 66; *Compt. chim.* 1851, 104.



The yellow die from the yellow wood of *Mactura tinctoria* (*Handb. viii. Phytochem.* 76). — Preisser's statements (p. 28; *Comp. Rev. scient.* 16, 57; *J. pr. Chem.* 32, 155).

*Preparation.* The decoction of the yellow wood is evaporated to a weight equal to that of the wood employed, and, after a day or two, the yellow sediment is collected on a filter; the filtrate concentrated and set aside, yields an additional quantity of this deposit, while morintannic acid remains in solution. On pressing the yellow sediment, dissolving it in boiling alcohol, and pouring the solution into ten times its volume of cold water, yellow-brown flocks of the lime-compound of morin are deposited; they may be purified by washing them with cold water, dissolving them three or four times in alcohol, and precipitating with water; 100 pts. of the lime-compound of morin thus obtained, are boiled with 12 pts. of oxalic acid crystals, and 15·60 pts. alcohol of 75 p. c.; the liquid is filtered at the boiling heat into 100 times its volume of water, and the morin, which separates in the form of a yellowish white crystalline powder, is redissolved in alcohol, reprecipitated by water, and dried at 100°, avoiding contact with the air. (Wagner.)

*Properties.* White crystalline powder, which acquires a faint yellow colour in contact with air (containing ammonia). Exhibits a slight acid reaction in solution. Has a slightly bitter not astringent taste. (Wagner.)

					Wagner.
					mean.
18 C .....	108	.....	55·10	.....	55·17
8 H .....	8	.....	4·08	.....	4·15
10 O .....	80	.....	40·82	.....	40·68
<hr/>					
$C^{18}H^8O^{10}$ ....	196	.....	100·00	.....	100·00

Isomeric with morintannic acid (p. 473). Dellfs (*Brit. Assoc. Rep.* 1861, pt. 2, 78) gives the formula  $C^{14}H^6O^6 + 2HO$ .

*Decompositions.* 1. Morin gives off water when heated to 180°; it does not undergo any further alteration at 250°, but blackens at about 300°, giving off carbonic acid, and yielding a distillate of carbolic acid and pyrocatechin (xi, 379), the latter of which solidifies in the crystalline form on cooling. — 2. It dissolves in *oil of vitriol*, with dark yellow-brown colour, and the odour of castoreum; the solution deposits a red body when warmed or left at rest, and decomposes when heated, giving off sulphurous and carbolic acids. — 3. With strong *nitric acid* it forms a red solution, which, when evaporated, gives off red vapours, and deposits large yellowish-white tables of styphnic acid. — 4. The aqueous solution of morin does not absorb *oxygen* from the air; but if mixed with *ammonia*, it turns brown, and blackens in contact with the air; acids then precipitate from it, not morin, but a humous substance, perhaps metagallic acid (p. 458). — 5. From *cupric acetate* or *sulphate*, it reduces cuprous oxide on boiling with potash. It reduces *nitrate of silver*, especially after addition of ammonia. (Wagner.)

*Combinations.* Morin dissolves in 4000 parts of cold, and in 1060 pts. of boiling water. It dissolves without colour in aqueous *sulphuric*,

*hydrochloric, phosphoric, acetic, oxalic, or tartaric acid.* It dissolves with yellow colour in *oil of vitriol*, and is precipitated by water. — It dissolves with fine yellow colour in aqueous solutions of *alkalis* and *alkaline carbonates*. Aqueous morin containing traces of fixed alkalis turns yellow in the air, from absorption of ammonia.

*Baryta-compound of Morin.* — When morin is boiled with recently precipitated carbonate of baryta and water, the filtrate leaves on evaporation, a red-brown powder, which, at 100° contains, on the average, 22.2 p. c. baryta, agreeing approximately with the formula  $C^{72}H^{32}O^{40}, 3BaO$ . (Wagner).

*Lime-compound.* — The lime-compound of morin, which is obtained from the decoction of yellow wood, and separates from alcohol in sulphur-yellow crystals, gives off 2 at. water at 100°, and then contains 6.83 p. c. lime, agreeing nearly with the formula  $2C^{18}H^8O^8, CaO, HO$  (calc. 7.12 p. c.  $CaO$ .) (Wagner).

Aqueous morin precipitates *alum-solutions* light yellow, after addition of ammonia.

*Lead-compound.* Alcoholic morin added to alcoholic acetate of lead, produces a light yellow precipitate, which becomes black-brown when dry, and contains 44.1, 45.6 to 47.2 p. c. lead-oxide. (Wagner.)

Aqueous morin forms a lemon-yellow precipitate with *protochloride of tin*. It precipitates *ferrous sulphate* olive-green, and colours *ferric chloride* garnet-red (or in presence of morintannic acid, blackish green.)

Morin dissolves easily in *alcohol*, forming a dark yellow solution, from which it is precipitated by water. It dissolves readily in *ether*. (Wagner.) According to Chevreul, it is precipitated from its aqueous solution by solution of *gelatin*; according to Wagner it is not.

## B.—Tannic Acids (and allied bodies) from Cinchona-barks.

### 1. Cinchonatannic Acid.



BERZELIUS. *Lehrbuch*, 3 Aufl. 6, 246.

PELLETIER & CAVENTOU. *Ann. Chim. Phys.* 15, 337.

R. SCHWARZ. *Wien. Akad. Ber.* 7, 249; *J. pr. Chem.* 56, 76; abstr. *Ann. Pharm.* 80, 330; *Pharm. Centr.* 1852, 193.

Cinchona-barks contain a tannic acid different from gallotannic acid, which imparts to them the property of precipitating tartar-emetic greyish yellow, imparting a green colour to ferric salts, and precipitating solution of gelatin. (Berzelius). — The tannin, both from brown and from red cinchona-bark precipitates ferric salts dark green; that from yellow cinchona bark forms a lighter green precipitate with ferric salts. (Pelletier & Caventou.) — Schwarz examined quinotannic acid prepared from *China regia*.

*Preparation.* 1. The decoction of cinchona bark is mixed with a small quantity of calcined magnesia, which precipitates cinchona-red; the filtrate is precipitated with neutral acetate of lead; the precipitate is decomposed under water by hydrosulphuric acid; the liquid filtered from the sulphide of lead (chinovin and a little cinchona-red) is precipitated with basic acetate of lead; the precipitate separated by filtration is dissolved in dilute acetic acid (which leaves cinchona-red undissolved), and the filtrate is precipitated by ammonia. The light yellow precipitate is washed and decomposed by hydrosulphuric acid, and the liquid filtered from the sulphide of lead is again precipitated with an alcoholic solution of neutral acetate of lead. If the cinchonatanate of lead thus obtained be decomposed under water by hydrosulphuric acid, and the liquid, filtered from the sulphide of lead, evaporated in vacuo over oil of vitriol and a mixture of ferrous sulphate and lumps of potash, cinchonatanic acid remains behind, already somewhat altered. (Schwarz.)—2. The bark is exhausted with water at 60°, containing 1 or 2 p. c. oil of vitriol; the filtrate is mixed with carbonate of potash, which throws down a compound of cinchonatanic acid with excess of quinine or cinchonine; and this compound is washed on the filter with a small quantity of water, during which it turns red in consequence of the oxidation of part of the tannic acid; it is then dissolved in dilute acetic acid, the oxidised extractive matter remaining in combination with the acetic acid; the liquid is precipitated with basic acetate of lead (the colourless solution retaining quinine and cinchonine, which may be further worked up); the precipitated cinchonatanate of lead is decomposed by hydrosulphuric acid; and the filtrate is evaporated in vacuo. (Berzelius.) Or the above-mentioned acid extract is boiled with hydrate of magnesia; the liquid is filtered; the residue containing magnesia, cinchonatanic acid, quinine, and cinchonine, is dissolved in dilute acetic acid; the solution filtered from the cinchona-red, is precipitated by basic acetate of lead; and the precipitate is decomposed as above. (Berzelius.)

The cinchonatanic acid obtained by method 2, may be purified by dissolving it in a small quantity of water, and evaporating the filtrate in vacuo,—or better by solution in ether and evaporation. (Berzelius.)

*Properties.* Light yellow, friable, very hygroscopic mass, which becomes electric by friction. Has a slightly sour, somewhat astringent taste, but is not at all bitter.

Calculation according to Schwarz.				Schwarz.	
42 C .....	252	.....	44.84	.....	44.75
30 H .....	30	.....	5.33	.....	5.49
35 O .....	280	.....	49.83	.....	49.76
<hr/>					
C <sup>42</sup> H <sup>30</sup> O <sup>35</sup> .....	562	.....	100.00	.....	100.00

Schwarz regards the substance analysed as a mixture of 2 at. oxidised tannic acid C<sup>14</sup>H<sup>10</sup>O<sup>12</sup>, and 1 at. unaltered tannic acid C<sup>14</sup>H<sup>8</sup>O<sup>9</sup> + 2aq.

*Decompositions.* 1. Cinchonatanic acid heated to 100° in a stream of carbonic acid, acquires a deep red colour; if water be then poured upon it, a red-brown resin separates. (Schwarz.) When subjected to dry distillation, it emits a faint odour of carbolic acid, and yields a distillate, which exhibits towards alkalis in contact with the air, and

towards ferric chloride, the same reactions as pyrocatechin (xi, 379). (Schwarz.)—2. Its aqueous solution, when evaporated by heat, deposits a red-brown powder; after the residue has been exhausted with water, a compound of cinchonatannic acid with cinchona-red remains undissolved; and finally the acid is completely converted into cinchona-red. (Berzelius.)—The aqueous solution of cinchonatannic acid, especially if supersaturated with alkalis or alkaline earths, absorbs oxygen, and acquires a darker colour. (Berzelius.) In this reaction, products are formed, which may be regarded as compounds of a body containing  $C^{10}H^7O^6$ , with oxygen and water. (Schwarz.)

*a.* Aqueous cinchonatannic acid deposits, on addition of water, a red-brown substance, which, when washed and dried at  $100^{\circ}$ , contains 55.35 p. c. carbon, 5.68 hydrogen, and 38.97 oxygen, and may be represented, according to Schwarz, by the formula  $C^{36}H^{22}O^{19}$ , or  $3C^{12}H^7O^6 + HO$ . (calc. 55.38 p. c. C., 5.64 H., and 38.98 O.) From the filtrate, dilute sulphuric acid separated red flocks, easily soluble in alcohol, and sparingly in water, and containing at  $100^{\circ}$ , 38.87 p. c. C., 4.81 H., and 56.32 O.: according to Schwarz =  $C^{12}H^9O^{13}$ , or =  $C^{12}H^7O^{11} + 2aq$ . (calc. 38.91 C., 4.86 H., and 56.23 O.)—*b.* Cinchonatannic acid in contact with air and ammonia, rapidly absorbs oxygen, then, on addition of dilute sulphuric acid, gives off carbonic acid—the volume of which, however, is less than that of the oxygen absorbed—and deposits red-brown flocks, probably consisting of cinchona-red.—*c.* Cinchonatanate of lead dried at  $100^{\circ}$ , in contact with the air, was found to contain 54.3 p. c.  $PbO$ , and, after deduction of this, 47.92 p. c. C., 4.85 H., and 47.23 O., showing that it had been converted into  $C^{12}H^7O^9$  (calc. 47.67 p. c. C., 4.63 H., and 47.70 O.). (Schwarz.)

3. Cinchonatannic acid, heated with aqueous *hydrochloric acid*, is decomposed, with separation of red flocks, which dissolve with leek-green colour in aqueous alkalis. (Schwarz.)—4. When heated with *potash-ley* it loses the power of precipitating gelatin, and does not recover that power even after supersaturation with acids. (Pelletier & Caventou.)

Cinchonatannic acid dissolves readily in *water*.

From the concentrated aqueous solution, *hydrochloric* and *sulphuric acids* throw down compounds of cinchonatannic acid with the acids, but less easily than from aqueous gallotannic acid. (Berzelius.)

It unites with *bases*, forming easily alterable salts, which split up into cinchona-red and a carbonate, especially if they contain excess of base. (Berzelius.) From a concentrated aqueous solution of cinchonatannic acid, *carbonate of potash* throws down a sparingly soluble compound which soon turns red. (Berzelius.)

*Cinchonatannate of Lead.* Preparation, see above. The salt, dried in vacuo over oil of vitriol and a moist mixture of ferrous sulphate and lumps of potash, contains 53.5 p. c. lead-oxide, and after deduction of this, 55.70 p. c. C., 4.60 H. and 39.70 O., and is, therefore,  $C^{28}H^{18}O^{15}$  (calc. 55.81 C., 4.31 H., 39.88 O.) +  $3PbO$ . (Schwarz.) The lead-salt dried at  $100^{\circ}$  contains 49.20 p. c. lead-oxide. (Reichhardt.)

Cinchonatannic acid dissolves easily in *alcohol* and *ether*. (Berzelius.) With *starch*, *gelatin*, and *white of egg*, it behaves like gallotannic acid. The aqueous solution mixed with the latter acid, dries up to a transparent extract. (Berzelius.)

## 2. Cinchona-red.

PELLETIER & CAVENTOU. *Ann. Chim. Phys.* 15, 315.

R. SCHWARZ. *Wien. Akad. Ber.* 7, 255.

REICHARDT. *Ueber die chemischen Bestandtheile der Chinarinden*, Braunsch. 1855.

*Oxidised Tannin of Cinchona-bark, Rouge cinchonique, Matière colorante rouge du Quinquina.* — Reuss (*Gött. Anz.* 1812, 601) first distinguished the non-bitter constituent, insoluble in water, of the alcoholic extract of cinchona-bark, by the name of *Rouge cinchonique*. The cinchona-red of Schwarz exhibits different properties from that of Pelletier & Caventou, the difference arising, according to Schwarz, from the presence of humous substances; but, according to Reichardt (*Wien. Akad. Ber.* 30, 169), pure cinchona-red was obtained only by Schwarz, whereas that of Pelletier & Caventou likewise contained quinovine. — Guiraud-Boissnot (*N. J. Pharm.* 25, 199) distinguished between soluble and insoluble cinchona-red.

*Formation.* From cinchonatanmic acid by oxidation (p. 481).

*Occurrence.* In brown, red and yellow cinchona-bark. (Pelletier & Caventou.) In *Cinchona regia*. (Schwarz.) Most abundantly in *Cinchona rubra*, less in *Cinchona regia* and *C. flava fibrosa*, not at all in Huanoco cinchona. (Reichardt.) According to Reichel (*Ueber Chinarrinden und deren chemischen Bestandtheile*, Leipz. 1856), it occurs also in the latter. The extract of *Cinchona rubra* prepared with water acidulated with sulphuric acid, deposits cinchona-red on standing. (Reichardt). — Cinchona-red occurs also in Carapa-bark from Cayenne, perhaps obtained from a *Personia* (Petroz & Robinet, *J. Pharm.* 7, 349). — A red colouring matter, obtained by Caventou (*N. J. Pharm.* 16, 300) from the bark of *Suilenia senegalensis* exhibits a certain degree of similarity to cinchona-bark.

*Preparation.* 1. Pelletier & Caventou exhaust the bark with alcohol; evaporate the tincture to dryness; boil the residue repeatedly, first with acidulated, then with pure water; and extract the fat with ether, the cinchona-red then remaining behind. — 2. The powder of *Cinchona rubra*, exhausted with water containing sulphuric acid and with ether, is digested four times with alcohol of 90 p. c., or as long as the alcohol runs away coloured; the tinctures are evaporated; and the residue is purified by re-solution in alcohol and evaporation (Reichardt).

3. The bark of *Cinchona regia*, previously exhausted with water, is digested with dilute aqueous ammonia; the red-brown liquid is precipitated with hydrochloric acid; the red-brown flocks containing quinovine and cinchona-red, are collected, washed, and boiled with thin milk of lime, a compound of quinovine and lime then passing into solution, whilst cinchona-red, together with lime, remains in the residue. This residue is washed with boiling water and decomposed by dilute sulphuric acid; the cinchona-red thus separated is thoroughly washed, redissolved in ammonia, and precipitated with hydrochloric acid; the precipitate is washed and dissolved in alcohol; and the solution filtered from the insoluble matter is evaporated to dryness (Schwarz).

4. Reichel exhausts Huanoco cinchona-bark with alcohol of 95 p. c. evaporates the extract to dryness, and exhausts successively all the constituents that are soluble in ether and in water.

*Properties.* Red-brown, inodorous, tasteless, infusible mass (Pelletier & Caventou, Reichhardt). Chocolate-brown (Schwarz), brick-red (Guiraud-Boissenot), light red-brown, darker when prepared from *Cinchona rubra* (Reichel).

Calculation according to Schwarz.				Schwarz. at 100°.
12 C .....	72	.....	53.33	..... 53.63
7 H .....	7	.....	5.19	..... 5.36
7 O .....	56	.....	41.48	..... 41.01
<hr/>				
C <sup>12</sup> H <sup>7</sup> O <sup>7</sup> .....	135	.....	100.00	..... 100.00

According to Guiraud-Boissenot, it consists of C<sup>14</sup>H<sup>8</sup>O<sup>6</sup>, with traces of iron and lime.

*Decompositions.* When moistened with water and heated, it gives off a beautiful purple-red vapour, condensing with the same colour,—then swells up, without actually melting, and yields a distillate consisting of a brown and afterwards black empyreumatic oil. The purple-red substance becomes more solid on cooling, then brown in contact with the air; it dissolves in alcohol, and is precipitated therefrom by water,—also in potash-ley, whence it is precipitated by acids, and with yellow colour in ether (Petroz & Robinet, *J. Pharm.*, 7, 355), Cinchona-red yields by dry distillation pyrogalllic acid, empyreumatic oil, and a carmine-coloured substance, soluble in ether and alcohol, insoluble in water (Guiraud-Boissenot).

Cinchona-red dissolves very slightly in boiling water, forming a pale yellow solution,—somewhat more freely in acidulated water (Pelletier & Caventou). It is insoluble in water, sparingly soluble in dilute acids (Reichhardt).—It dissolves abundantly in aqueous ammonia, potash and soda, whence it is precipitated by acids.—The ammoniacal solution forms with chloride of calcium a precipitate of a fine red colour (Reichhardt, Reichel). With magnesia and alumina it forms fine red lakes, the solutions of which in acids do not precipitate gelatin. From the solution in acetic acid it is precipitated by basic acetate of lead (Pelletier & Caventou). The aqueous solution (Pelletier & Caventou) and the ammoniacal solution (Reichhardt) yield with tartar-emetic, a precipitate of a fine red colour.

Cinchona-red is insoluble in alcohol. According to Reichel, it is more or less soluble in alcohol, according to the variety of the bark and the mode of preparation.

Insoluble or very slightly soluble in ether (Pelletier & Caventou and others). Dissolves easily in ether, forming a dark red solution (Schwarz). Dissolves easily in strong acetic acid, and is precipitated therefrom for the most part by water (Pelletier & Caventou, Reichhardt).

In the unaltered state, it is not precipitated by animal gelatin (Pelletier & Caventou), but its ammoniacal solution is precipitated thereby, after a while, on addition of alcohol (Reichhardt).—The solution of cinchona-red in aqueous potash or soda precipitates gelatin,

but not if it has been heated. On the other hand, cinchona-red, mixed with ammonia, baryta or lime, precipitates gelatin, after being heated, but not before (Pelletier & Caventon).

### 3. Lignoïn.



REICHE. *Ueber Chinarinden und deren Bestandtheile*, Leipzig, 1856.  
O. HESSE. *Ann. Pharm.* 109, 341.

The humous constituent of Huanoco cinchona bark,

*Cinchona-bark* exhausted with ether, alcohol and water, is repeatedly digested with soda-ley; the dark red-brown solution is precipitated with hydrochloric acid; the precipitate is washed, redissolved in soda-ley, and reprecipitated by dilute sulphuric acid; and this precipitate is washed, first with acidulated, then with pure water, and dried at 100° (Reichel).

*Properties.* Black-brown, easily friable mass, having but little lustre.

				Hesse. mean.
40 C .....	240 .....	59.25 .....	59.36	
23 H .....	23 .....	5.67 .....	5.86	
N .....	14 .....	3.47 .....	3.52	
16 O .....	128 .....	31.61 .....	31.26	
<hr/>				
$C^{40}H^{23}NO^{16}$ .....	405 .....	100.00 .....	100.00	

After deduction of 1.79 p. c. ash. — From *Cinchona rubra*, Reichel (*N. Br. Arch.* 92, 9) likewise obtained lignoïn, which however was found by analysis to contain 61.5 p. c. C., 4.65 H. and N., besides oxygen.

Lignoïn, boiled with *potash*, gives off ammonia (Hesse); melted with *potash*, it likewise emits the odour of woodruff (Reichel). — It dissolves quickly in aqueous *ammonia* and in *soda-ley* (Reichel); also in aqueous *alkaline carbonates*, without taking up oxygen (Hesse). The ammoniacal solution is precipitated by *acids*, and throws down from *lime-* and *baryta-salts* a red brown jelly,—from *lead-salts*, a light flesh-coloured precipitate (Reichel).

It is perfectly soluble in *alcohol* of 85 p. c. (Reichel).

### 4. Quinovatannic Acid.



HLASIWETZ. *Wien. Akad. Ber.* 6, 266; abstr. *Ann. Pharm.* 79, 130.

*Occurrence.* In the bark of *Cinchona nova* or *surinamensis*.

*Preparation.* The aqueous decoction of the bark is precipitated with neutral acetate of lead; the precipitate, which serves for the preparation of quinoa-red, is removed; and the filtrate is divided into three parts, one of which is completely precipitated with basic acetate of lead, and then mixed with the other two portions. The precipitate thus produced, containing quiovine, the remainder of the quinoa-red, and a small quantity of quinovatannic acid (but scarcely available for the preparation of the latter), is also removed, and the liquid filtered therefrom is precipitated with basic acetate of lead. The washed precipitate is decomposed under water by hydrosulphuric acid; the sulphide of lead is removed by filtration, and the hydrosulphuric acid, partly by warming the liquid, then completely by neutral acetate of lead; the liquid is again filtered; and the filtrate is mixed with a large quantity of strong alcohol, which throws down flocks of quinovatannate of lead. From this salt the acid is separated by hydrosulphuric acid, and the solution freed from sulphide of lead is evaporated in a stream of carbonic acid.

Amber-yellow, transparent, friable mass, having an astringent and somewhat bitter taste.

at 100°.				Hlasiwetz.
				mean.
28 C .....	168	.....	52.01	..... 51.82
19 H .....	19	.....	5.88	..... 5.85
17 O .....	136	.....	42.11	..... 42.33
<hr/> 2C <sup>14</sup> H <sup>9</sup> O <sup>8</sup> + aq. ....				323 ..... 100.00 ..... 100.00

*Decompositions.* 1. When mixed with *alkalis*, it oxidises in contact with the air. — The aqueous solution left for some time in contact with the air deposits a red powder, soluble in ammonia and in alcohol, and probably consisting of quinoa-red. — 2. By boiling for some time with dilute *sulphuric acid*, it is decomposed, with formation of a substance which reduces an alkaline solution of cupric oxide, like glucose. — 3. In contact with *cupric hydrate* or *acetate*, it assumes a dark-greenish brown colour, the protoxide of copper being reduced to dioxide, and the acid oxidised to viridic acid. — 4. It reduces *silver*- and *gold-salts*.

*Combinations.* Soluble in *water*. Turns brown in contact with *ammonia*, the colour gradually becoming darker. Does not precipitate *tartar-emetic*.

*Quinovatannate of Lead.* The aqueous acid does not precipitate neutral acetate of lead. The salt is prepared: 1. By precipitating the acid with basic acetate of lead, washing and drying at 100°. — 2. By precipitating the alcoholic solution of the acid with alcoholic sugar of lead, washing the precipitate, and drying at 100°.

According to 1.		Hlasiwetz.	According to 2.		Hlasiwetz.
					mean.
140 C .....	30.12	.... 29.99	28 C ....	26.25	.... 26.41
89 H .....	3.18	.... 3.08	17 H .....	2.65	.... 2.67
79 O .....	22.69	.... 22.67	15 O .....	18.75	.... 18.95
11 PbO ....	44.01	.... 44.26	3 PbO ....	52.35	.... 51.97
<hr/>			<hr/>		
100.00		.... 100.00	100.00		.... 100.00



No. 1 is regarded by Hlasiwetz as  $10C^{14}H^8O^7 + 11PbO + 9aq.$ ; No. 2, as  $2(C^{14}H^8O^7, PbO) + PbO, HO.$ —A third lead-salt contained  $4C^{14}H^8O^7, PbO.$  (*Wien. Akad. Ber.* 6, 270.)

Quinovatannic acid colours *ferric hydrochlorate* dark green.

It dissolves in *alcohol*, not in *ether*. Does not precipitate *solution of gelatin*.

## 5. Quinova-red.



PELLETIER & CAVENTOU (1820). *J. Pharm.* 7, 111.

HLASIWETZ. *Wien. Akad. Ber.* 6, 273; *Ann. Pharm.* 79, 138.

Different from cinchona-red. Occurs ready-formed in large quantity in *Cinchona nova*.

*Formation.* By the oxidation of quinovatannic acid (p. 485).

*Preparation.* 1. The aqueous decoction, or the alcoholic extract of the bark, is precipitated with neutral acetate of lead; the precipitate (which contains scarcely any organic compound except quinova-red) is decomposed under water by hydrosulphuric acid; and the mixture of quinova-red and sulphide of lead is washed with water and boiled with a small quantity of alcohol. From the alcoholic filtrate, the quinova-red is precipitated by the addition of a large quantity of water (Hlasiwetz). — 2. The bark is digested with dilute aqueous ammonia, the filtrate is precipitated with hydrochloric acid; and the precipitate is washed till the filtrate no longer turns iron-salts green, and therefore no longer contains quinovatannic acid. The residue is freed from admixed quinovine by boiling it 4 or 5 times with milk of lime; the compound of quinova-red with lime, which is insoluble in water, is decomposed by hydrochloric acid; the separated quinova-red is washed with water, and dissolved in dilute aqueous ammonia; and the solution is precipitated with hydrochloric acid. After washing out the hydrochloric acid with hot water, the precipitate is dissolved in alcohol, separated from the undissolved matter, and the pure quinova-red is precipitated by mixing the filtrate with water (Hlasiwetz).

*Properties.* Nearly black, shining resinous mass, yielding a dark red powder (Hlasiwetz).

at 100°.				Hlasiwetz.	
12 C .....	72 .....	61.01 .....	61.21 .....	61.21	
6 H .....	6 .....	5.09 .....	5.08 .....	5.08	
5 O .....	40 .....	33.90 .....	33.91 .....	33.91	
<hr/>				<hr/>	
$C^{12}H^6O^5$ .....	118 .....	100.00 .....	100.00 .....	100.00	

O. Hesse (*Ann. Pharm.* 109, 342) suggests the formula  $C^{10}H^{20}O^{16}$  (calc. 61.85 p.c. C., 5.17 H., 32.98 O), having regard to that of lignoïn (p. 484.)

By successive treatment with *potash* and *acids*, quinova-red is converted into a tannic acid (Pelletier & Caventou).—With *nitric acid* it forms oxalic acid (Pelletier & Caventou).

Quinova-red is nearly insoluble in *water*. (Hlasiwetz.) It is not altered by dilute acids. It dissolves easily in aqueous *ammonia*, and in the *fixed alkalis* (Hlasiwetz), less easily than chinchona-red. (Pelletier & Caventou.) Forms insoluble compounds with *baryta* and *lime*. (Hlasiwetz). Does not precipitate *tartar-emetic* (Pelletier & Caventou).

Alcoholic quinova-red is completely precipitated by alcoholic *sugar of lead*. The red-brown precipitate washed and dried at 100°, contains 45.1 p. c. PbO, 32.61 C., and 2.33 H., and, therefore, consists of oxide of lead and oxidised quinova-red  $C^{24}H^{10}O^{11}$  (Hlasiwetz).

Quinova-red dissolves easily in *alcohol* and in *ether*. (Hlasiwetz.)

### C.—Tannic Acids from *Pinus Sylvestris* and *Phlobaphene*.

#### 1. Oxypinitannic Acid.



KAWALIER. *Wien. Akad. Ber.* 11, 354.

Occurs about Christmas in the needles of *Pinus sylvestris*, and is obtained as a lead-salt in the preparation of pinipicrin (see below). The lead-salt is digested with acetic acid diluted with 8 pts. water; the filtrate is precipitated with basic acetate of lead, which throws down a pure lead-salt; the washed precipitate is decomposed by hydro-sulphuric acid; and the filtrate is evaporated over the water-bath.

Grey or brownish powder. Inodorous. Has a very astringent taste.

at 100°.				Kawalier.
14 C.....	84	.....	51.22	..... 51.24
8 H.....	8	.....	4.87	..... 4.98
9 O.....	72	.....	43.91	..... 43.78
$C^{14}H^{18}O^9$ .....	164	.....	100.00	..... 100.00

After deduction of 1.6 p. c. ash.

*Decomposition.* 1. Burns when heated on platinum-foil, leaving a residue of charcoal.—2. After supersaturation with ammonia, it quickly absorbs *oxygen* from the air, and becomes dark-brown.—3. By boiling with *hydrochloric acid*, it becomes turbid, and acquires the colour of carmine. Aqueous oxypinitannic acid, mixed with *oil of vitriol*, turns red, and deposits flocks on addition of water. On boiling it with dilute sulphuric acid, a red powder is precipitated, and after the removal of this powder and the acid, there remains in solution an amorphous substance, which contains 42.60 p. c. C., and 6.80 H., and does not consist of sugar (Rochleder & Kawalier, *Wien. Akad. Ber.* 29, 22).—4. The *ammonia-salt*, mixed with *nitrate of silver*, becomes brown-red, and separates metallic silver when heated.

*Combinations.* The acid dissolves readily in *water*. The aqueous acid is coloured yellow by *ammonia*, and forms with *baryta-water*, a yellow liquid, which deposits red flocks when heated. It is coloured green by *ferric chloride*, and precipitates greenish-brown by sulphate of copper, and a small quantity of ammonia. It is not precipitated by *tartar-emetic* or *nitrate of silver*.

*Oxypinitannate of Lead.*—Neutral acetate of lead forms, with the aqueous acid, a lemon-yellow precipitate, inclining to greenish; basic acetate of lead, a cream-coloured precipitate. Preparation as above.

				Kawalier.	
28 C	168	.....	26.43	.....	26.11
13 H	13	.....	2.05	.....	2.08
15 O	120	.....	18.86	.....	18.48
3 PbO	335	.....	52.66	.....	53.33
<hr/>				<hr/>	
C <sup>28</sup> H <sup>13</sup> O <sup>15</sup> , 3PbO	636	.....	100.00	.....	100.00

## 2. Pinitannic Acid.



KAWALIER. *Wien. Akad. Ber.* 11, 357. — 29, 19.

1. Occurs about Christmas in the needles of old trees of *Pinus sylvestris*, and is obtained as a lead-salt in the preparation of pinipicrin. The liquid from which the oxypinitannic acid has been precipitated by neutral acetate of lead, is heated to the boiling point, basic acetate of lead is then added by drops, and the whole left to cool. The washed precipitate is decomposed by hydrosulphuric acid, and the liquid heated with the sulphide of lead, then filtered and evaporated to dryness in a stream of carbonic acid.

2. It occurs also\* in the green parts of *Thuja occidentalis*. (See *Thujigenin*.) It is partly precipitated, together with thujin, by neutral acetate of lead, partly, together with thujigenin, in the subsequent precipitation by basic acetate of lead, and remains in solution when these precipitates are decomposed by hydrosulphuric acid, and the thujin and thujigenin have crystallised out. The remaining solutions are evaporated to dryness, and the pinitannic acid is extracted by anhydrous ether-alcohol. The filtrate quickly evaporated to dryness over the water-bath, leaves the acid which may be dried in vacuo over oil of vitriol.

Yellow-red, or, if prepared from *Thuja*, brownish yellow powder, having a slightly bitter, astringent taste. At 100° it becomes soft and glutinous.

				Kawalier.	
				from <i>Pinus.</i> from <i>Thuja.</i>	
14 C	84	.....	53.84	.....	53.67
8 H	8	.....	5.12	.....	5.55
8 O	64	.....	41.04	.....	40.78
<hr/>				<hr/>	
C <sup>14</sup> H <sup>8</sup> O <sup>8</sup>	156	.....	100.00	.....	100.00

*Decompositions.* 1. Burns on platinum-foil, leaving charcoal.— 2. Swells up at  $130^{\circ}$ , yields an acid watery distillate between  $100^{\circ}$  and  $200^{\circ}$ , and tar at higher temperatures.— 3. The ammoniacal solution absorbs oxygen and becomes red-brown.— 4. When aqueous pinitannic acid is heated with dilute acids, a red powder is separated, while an amorphous substance remains behind.

*a.* The red powder (prepared with pinitannic acid from pines) contains 58.22 p. c. C., 4.65 H., and 37.13 O., agreeing with the formula  $C^{42}H^{28}O^{20}$  (calc. 58.33 C., 4.63 H., and 37.04 O.).— The product from *Thuja*, after washing with cold water, dissolves with difficulty in boiling water, and separates in brick-red flocks on cooling. After drying in vacuo, it contains, on the average, 58.37 p. c. C., 4.69 H., and 36.94 O.

*b.* The liquid freed from the red powder and the acid, leaves, when evaporated over the water-bath, an amorphous, brown-yellow residue, which reduces cupric oxide in alkaline solution, like glucose, but does not taste sweet or exhibit any of the other characters of a sugar. It contains 47.02 p. c. C., 5.84 H., and 47.14 O., answering to the formula  $C^{12}H^9O^9$  or  $C^{26}H^{21}O^{21}$ .

Pinitannic acid dissolves readily in water. The solution colours ferric chloride dark brown-red, and precipitates cupric sulphate and nitrate of silver, the latter on addition of ammonia.

*Pinitannate of Lead.*— The aqueous acid throws down from neutral acetate of lead, a yellow precipitate, easily soluble in a small quantity of free acetic acid; from the basic acetate, at mean temperature, a lemon-yellow at the boiling heat, and with excess of basic acetate, a fiery chrome-yellow precipitate. Contains 54.16 p. c. lead-oxide, and after deduction of this, 53.11 p. c. C., 5.42 H., and 41.47 O., on which account Kawalier supposes it to contain  $C^{58}H^{33}O^{33} = 4C^{14}H^8O^8 + HO$  in combination with lead-oxide (calc. 53.08 C., 5.21 H., and 41.71 O.).

Pinnitannic acid dissolves easily in alcohol and ether. It does not precipitate solution of gelatin. Its aqueous solution, heated to boiling with a small quantity of stannic hydrochlorate, communicates to woollen stuffs mordanted with alum or tin-salt, a permanent lemon-yellow to chrome-yellow colour.

### 3. Cortepinitannic Acid.



KAWALIER. *Wien. Akad. Ber.* 11, 363.

*Occurrence.* In the inner and outer bark of old trees of *Pinus sylvestris* about Christmas.

*Preparation.* From the inner bark (see *Pinicorretin*, p. 33). The lead-salt obtained in the preparation of pinicorretin is suspended in water, and decomposed by hydrosulphuric acid; and the heated liquid is filtered from the sulphide of lead, and evaporated to dryness in a stream of carbonic acid.

2. *From the outer bark.* The bark, cleansed and coarsely bruised, is boiled with alcohol of 40°; the filtrate is left to cool; the wax which separates is removed by filtration; and the greater part of the alcohol is distilled off, whereupon a fresh quantity of wax separates out. The filtered and expressed liquid, mixed with water and solution of neutral acetate of lead, yields a precipitate of impure cortepinitannate of lead ( $\alpha$ ); and the liquid filtered therefrom yields, with basic acetate of lead, a second precipitate, which has a dirty yellow colour, but likewise consists of cortepinitannate of lead ( $\beta$ ). The first lead-salt is treated with dilute acetic acid; the red filtrate is precipitated with basic acetate of lead; the brown-red precipitate is washed and decomposed by hydrosulphuric acid; and the hot-filtered liquid is evaporated to dryness in a stream of carbonic acid, cortepinitannic acid then remaining.

*Properties.* Bright-red powder.

					Kawalier.	
					<i>a.</i>	<i>b. mean.</i>
32 C	.....	192	....	55.65	....	56.12
17 H	.....	17	....	4.92	....	4.76
17 O	.....	136	....	39.43	....	39.12
$C^{32}H^{17}O^{17}$ ....					345	....
					100.00	....
					100.00	....
					100.00	....

*a.* Obtained from the inner; *b.* from the outer bark. For *b*, Kawalier gives the formula  $C^{64}H^{33}O^{33}$ , differing from the formula above by  $\frac{1}{2}$  at. water, and regards *a* as  $2C^{16}H^7O^7 + 3HO$ , *b* as  $4C^{16}H^7O^7 + 5HO$ .

*Decompositions.* The lead-salt  $\beta$ , obtained as above, contains in 100 pts. after deduction of the lead-oxide, 54.61 p. c. C., 5.18 H., and 41.21 O., therefore cortepinitannic acid,  $C^{16}H^9O^9$  (calc. 54.24 p. c. C., 5.08 H., 40.68 O.), combined with lead-oxide (such, at least, appears to be Kawalier's meaning). When this lead-salt is decomposed under water by hydrosulphuric acid, and the filtrate is evaporated in contact with the air, there remains an apparently unaltered residue, which however contains 48.68 p. c. C., 4.95 H., and 46.37 O., and is therefore perhaps pinicortannic acid  $C^{32}H^{19}O^{23}$ .

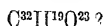
The aqueous solution of the acid is coloured green by *ferric chloride*.

*Cortepinitannate of Lead.*—Obtained from the inner bark in the manner described at page 33.

					<i>In vacuo.</i>	
					Kawalier.	
48 C	.....	288	.....	34.69	.....	34.17
23 H	.....	23	.....	2.77	.....	2.86
23 O	.....	184	.....	22.17	.....	21.99
3 PbO	.....	335	.....	40.37	.....	40.98
$C^{48}H^{23}O^{23}, 3PbO$ .....					830	.....
					100.00	.....
					100.00	.....

After deduction of the lead-oxide,  $C^{48}H^{23}O^{23}$  or  $3C^{16}H^7O^7 + 2HO$ . (Kawalier.)

## 4. Pinicortannic Acid.



KAWALIER. *Wien. Akad. Ber.* 11, 360.

*Occurrence.* In the bark of *Pinus sylvestris*.

*Formation.* Cortepinitannic acid changes to pinicortannic acid when its solution is evaporated in contact with the air (see p. 490).

*Preparation.* See Pinnicorretin (p. 33).

*Properties.* Red-brown powder.

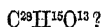
<i>In vacuo.</i>				Kawalier.
32 C .....	192 .....	48.60 .....	48.57	
19 H .....	19 .....	4.81 .....	4.93	
23 O .....	184 .....	46.59 .....	46.50	
<hr/>				
$\text{C}^{32}\text{H}^{19}\text{O}^{23}$ ....	395 .....	100.00 .....	100.00	

After deduction of 1.2 p. c. ash. —  $\text{C}^{32}\text{H}^{19}\text{O}^{23}$  or  $2\text{C}^{16}\text{H}^9\text{O}^{11}$  + aq. (Kawalier.)

When boiled with *water containing hydrochloric acid*, it is converted into a bright red powder, which, after drying in *vacuo*, contains 51.56 p. c. C., 4.47 H., and 43.97 O., and is therefore  $\text{C}^{48}\text{H}^{25}\text{O}^{31}$ , or  $3\text{C}^{16}\text{H}^8\text{O}^{10} + \text{HO}$  (Kawalier). Calc. 51.34 C., and 4.45 H.

After drying, it dissolves, but very slowly, in *water*. Its aqueous solution colours *ferric chloride*.

## 5. Tannopic Acid.



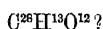
ROCHLEDER & KAWALIER. *Wien. Akad. Ber.* 29, 22.

Occurs in spring in the needles of *Pinus sylvestris*, and was obtained, instead of oxypinitannic acid, in a preparation undertaken with the object of obtaining the latter (p. 487). — Needles gathered about Easter contained tannopic acid; those gathered about Christmas yielded oxypinitannic acid.

It *oxidises* readily, especially in contact with warm moist air. When heated with *sulphuric* or *hydrochloric acid*, it yields a red decomposition-product, similar to that which pinitannic acid deposits under the same circumstances.

<i>at 100°.</i>				Kawalier.
28 C .....	168 .....	58.54 .....	58.45	
15 H .....	15 .....	5.22 .....	5.28	
13 O .....	104 .....	36.24 .....	36.27	
<hr/>				
$\text{C}^{28}\text{H}^{15}\text{O}^{13}$ .....	287 .....	100.00 .....	100.00	

## 6. Tannecortepinic Acid.



ROCHLEDER & KAWALIER. *Wien. Akad. Ber.* 29, 23.

*Occurrence.* In the bark of *Pinus sylvestris*, when the trees are between 20 and 25 years old.

*Preparation.* The chopped bark is thoroughly boiled with alcohol of 40°; the alcohol is completely distilled off (the last portions, after dilution of the residue with water); the viscid resin which separates from the residue is removed by filtration; the filtrate precipitated with neutral acetate of lead; the precipitate collected and washed; and the filtered liquid mixed with basic acetate of lead, whereby a fresh precipitate is formed, containing tannecortepinate of lead, like the first.

a. The precipitate formed by neutral acetate of lead is treated three times with quantities of dilute acetic acid insufficient for complete solution; the liquid is filtered from the undissolved portion, resin then remaining; the united acetic acid solutions are precipitated with basic acetate of lead; and the precipitate is collected, washed, and decomposed under water with hydrosulphuric acid. The liquid filtered from the sulphide of lead, and evaporated to half its volume in a stream of carbonic acid, deposits brown-red crusts of tannecortepinic acid.

b. The precipitate formed by basic acetate of lead is decomposed under water with hydrosulphuric acid; the filtrate is evaporated in a stream of carbonic acid; the residue is dissolved in alcohol, the solution precipitated with alcoholic neutral acetate of lead; the precipitate washed and decomposed under water with hydrosulphuric acid; the filtrate again evaporated in a stream of carbonic acid; and the residue dried at 100°.

*Properties.* Reddish brown powder, which does not become glutinous at 100°. Has an astringent taste.

				Kawalier.
				mean.
28 C .....	168	.....	60.65	..... 60.42
13 H .....	13	.....	4.69	..... 4.76
12 O .....	96	.....	34.66	..... 34.82
<hr/>				<hr/>
$\text{C}^{26}\text{H}^{13}\text{O}^{12}$ .....	277	.....	100.00	

After deduction of 0.14 to 0.8 p. c. ash.

The aqueous solution, heated with dilute *sulphuric* or *hydrochloric acid*, deposits a fine red precipitate of nearly the same composition as tannecortepinic acid. The filtrate freed from sulphuric acid and the rest of the red body, by a small quantity of basic acetate of lead, and from lead by hydrosulphuric acid, leaves, on evaporation, a sweetish colourless residue, which reduces an alkaline cupric solution,

like glucose, and burns on platinum with an odour of sugar. The quantity obtained from 100 pts. of tannecortepinic acid reduces as much cupric oxide as 5.43 pts. of grape-sugar.

With aqueous *ferric hydrochlorate* it becomes dark green, then red-brown, and finally yields a black-green precipitate.

## 7. Pityxylonic Acid.

WITTSTEIN. *Pharm. Viertelj.* 3, 14.

From *πικύς*, pine, and *ξύλον*, wood. — Occurs in the stem of *Pinus sylvestris*, and probably also in that of *Pinus Abies*.

*Preparation.* Finely rasped pine-wood is boiled with water, the liquid is mixed with carbonate of baryta, strained and evaporated to a few ounces, then filtered, and the residue is exhausted with ether. The mass exhausted with ether and treated with warm alcohol, yields to the latter liquid pityxylonic acid, which remains behind when the solution is evaporated.

Brown-yellow, amorphous mass, hygroscopic, with a strong bitter taste and acid reaction.

Sparingly soluble in cold, easily in boiling water, forming a pale yellow solution, which becomes turbid on cooling. — Easily soluble in alkaline water.

*Lead-salt.* The acid is dissolved in ammoniacal water; and the solution precipitated with neutral acetate of lead. — Bitter powder, becoming electric by friction. — Somewhat soluble in water.

	at 100°.		Wittstein. mean.
25 C .....	150.0 .....	44.43 .....	44.58
20 H .....	20.0 .....	5.92 .....	5.81
8 O .....	64.0 .....	18.99 .....	19.11
PbO .....	111.8 .....	30.66 .....	30.50
<hr/>			
C <sup>25</sup> H <sup>20</sup> O <sup>8</sup> , PbO ...	345.8 .....	100.00 .....	100.00

So according to Wittstein.

## 8. Phlobaphene.



STÄHELIN & HOFSTETTER. *Ann. Pharm.* 51, 65.

According to Stähelin & Hofstetter, phlobaphene is an ordinary constituent of the outer bark of *Pinus sylvestris*, *Betula alba*, yellow cinchona-bark, and the bark of *Platanus acerifolia*. Kavalier (*Wien. Akad. Ber.* 11, 344) contests the independent existence of phlobaphene, whereas J. Wolff (*Pharm. Viertelj.* 3, 1) finds it also in birch-fungus, and Wittstein (*Pharm. Viertelj.* 3, 10) in pine-bark. Hesse (*Ann. Pharm.* 109, 343) calls attention to the resemblance of phlobaphene to cinchona-red (p. 482),



whereas, according to others, it resembles rhodoxanthin. Finding it impossible to determine the precise relations of these imperfectly investigated bodies, I have thought it best to follow Stähelin & Hofstetter. (Kr.)

By the following mode of treating the barks, sometimes phlobaphene is obtained, sometimes bodies differing from it by water or oxygen.

I. *Phlobaphene from the outer Bark of Pinus sylvestris*.—From the alcoholic extract of the bark previously exhausted with ether, ether extracts wax, leaving a brown residue insoluble in water.

a. When the brown residue (or phlobaphene obtained by 1, b) is dissolved in aqueous ammonia, and the solution precipitated with dilute sulphuric acid, red-brown flocks are thrown down, and the yellow filtrate, on exposure to the air, deposits an additional quantity of the same substance. These flocks contain 59.98 p. c. C., 4.44 H., and 35.58 O., and consist of Stähelin & Hofstetter's hydrate of phlobaphene  $C^{20}H^8O^8 + aq.$ —The same hydrate of phlobaphene is likewise extracted by aqueous alkalis from the bark previously exhausted with ether and alcohol, and is precipitated from the red-brown solution by sulphuric acid. After repeated solution in alcohol and evaporation, it contains 59.58 p. c. C., 4.59 H., and 35.83 O.; it is insoluble in water and dilute acids, precipitated from the ammoniacal solution by baryta- and lime-salts, and sparingly soluble in alcohol after drying.

b. When the ammoniacal solution of the brown residue is treated with neutral acetate of lead, the precipitated lead-salt exhibits the composition  $\alpha$  or  $\beta$ , according to the circumstances of the preparation.

<i>Lead-salt <math>\alpha</math>.</i>				Stähelin & Hofstetter.
60 C.....	360.0	.....	34.84	..... 35.25
25 H.....	25.0	.....	2.42	..... 2.70
25 O.....	200.0	.....	19.36	..... 19.90
4 PbO .....	447.2	.....	43.38	..... 42.15
$3C^{20}H^8O^8, 4PbO + aq.$ ....				1032.2 ..... 100.00 ..... 100.00
<i>Lead-salt <math>\beta</math>.</i>				Stähelin & Hofstetter.
20 C .....	120.0	.....	18.01	..... 18.09
11 H .....	11.0	.....	1.65	..... 1.80
11 O .....	88.0	.....	13.21	..... 13.20
4 PbO .....	447.2	.....	67.13	..... 66.91
$C^{20}H^8O^8, 4PbO + 3aq.$ .....				666.2 ..... 100.00 ..... 100.00

c. When the brown residue is dissolved in a small quantity of boiling alcohol, and precipitated with hot water, the liquid being stirred, a red-brown precipitate of phlobaphene is produced while tannic acid remains dissolved in the filtrate.—The phlobaphene immediately separated by filtration, and washed with boiling water, is red-brown, free from nitrogen, tasteless, and unalterable in the air, both in the moist and in the dry state. It does not melt when heated, but burns with a smoky flame, leaving a large quantity of charcoal. It is slightly soluble in acetic acid, insoluble in water and in other dilute acids, but dissolves readily in aqueous alkalis, with deep brown-red colour, and after drying, is no longer soluble in alcohol. It con-

tains, on the average, 62.78 p. c. C., 4.30 H., and 32.92 O., answering to the formula  $C^{20}H^8O^8$  (calc. 62.50 C., 4.16 H., and 33.34 O.).

d. The yellow, sour and astringent liquid filtered from the phlobaphene, deposits, on standing or evaporation in contact with the air, hydrate of phlobaphene, in the form of a red-brown powder, containing 59.81 p. c. C., 4.59 H., and 35.60 O. It precipitates metallic and earthy salts, also ferric chloride, the latter dark-green. On adding neutral acetate of lead to the hot liquid immediately after filtration, a grey precipitate is formed, containing, on the average, 37.92 p. c. C., 2.49 H., 24.80 O., and 34.79 PbO., answering to the formula  $C^{20}H^8O^{10}, PbO$ .

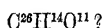
II. *Phlobaphene from the Bark of Platanus Acerifolia*.—Extracted by dilute potash-ley from the bark previously exhausted with ether, and precipitated by dilute sulphuric acid. The red-brown flocks are washed, then dissolved several times in boiling alcohol, and the solution is evaporated. Red-brown amorphous powder, having a slightly astringent taste, somewhat soluble in cold, more soluble in boiling water; soluble in aqueous ammonia and in alcohol. Contains, on the average, 57.23 p. c. C., 4.80 H., and 37.97 O., corresponding to the formula  $C^{20}H^8O^8 + 2aq$ . (calc. 57.14 C., 4.76 H., and 38.10 O.).

III. *Phlobaphene from Yellow Cinchona-bark*.—When the alcoholic extract of the bark, previously exhausted with ether, is evaporated as long as it remains clear, and then mixed with water containing sulphuric acid, a copious red-brown precipitate falls to the bottom. From this precipitate an insoluble portion,  $C^{21}H^{12}O^7$ , may be separated by digestion in ammonia. If the solution be then precipitated with acetic acid, and the precipitate treated with alcohol, phlobaphene remains behind, and a fresh portion of the body  $C^{21}H^{12}O^7$  passes into solution. The phlobaphene thus obtained is a brown-red powder, which does not fuse when heated, is insoluble in water, acids, alcohol, and ether, and dissolves easily in aqueous alkalis. It contains 62.55 p. c. C., 4.41 H., and 33.04 O., answering to the formula  $C^{20}H^8O^8$ , and the compound precipitated by neutral acetate of lead from its ammoniacal solution, contains 18.57 p. c. C., 1.39 H., 10.19 O., and 69.85 PbO, agreeing with the formula  $C^{20}H^8O^8, 4PbO$ . From the cinchona-bark exhausted with alcohol and ether, dilute potash-solution extracts hydrate of phlobaphene, precipitable by sulphuric acid, and containing 59.35 p. c. C., 4.59 H., and 36.06 O. When this compound is precipitated from the alcoholic solution by alcoholic sugar of lead, the precipitate contains, on the average, 70.28 p. c. PbO, as required by the formula  $C^{20}H^8O^8, 4 PbO$  (calc. 69.77 PbO).

IV. *Phlobaphene from the outer Bark of Betula Alba*.—After this bark has been exhausted with ether, alcohol extracts phlobaphene containing 62.37 p. c. C., 4.35 H., and 33.28 O. Hydrate of phlobaphene then remains in the bark, whence it may be extracted by potash-ley, and when precipitated by hydrochloric acid, contains 59.87 p. c. C., 4.67 H., and 35.46 O.

D.—Tannic Acids from *Aspidium Filix Mas.*

## 1. Tannaspidic Acid.



LUCK. *Jahrb. pr. Pharm.* 22, 159; abstr. *Pharm. Centr.* 1851, 657 and 676; *Chem. Gaz.* 1851, 452 and 467.

*Occurrence.* In the root of *Aspidium Filix mas.*

*Preparation.* When the coarsely pulverised fern-root is boiled with alcohol of 75 to 80 p. c., and the decoction mixed with water, a little hydrochloric acid, and pulverised sulphate of soda, a precipitate is formed, containing tannaspidic and pteritannic acids. This precipitate is collected, washed with solution of sulphate of soda, pressed, again triturated with water, and digested for half an hour at 60° — 80° with water containing hydrochloric acid, whereby ammonia and other bases are removed. The residue, washed with water, dried and exhausted with ether free from alcohol, yields pteritannic acid to this solvent. The ethereal solution is filtered; the residue warmed with strong alcohol, mixed with a few drops of solution of neutral acetate of lead, then with hydrosulphuric acid (which renders it capable of filtration), and filtered; and the filtrate is evaporated, first in a stream of hydrogen, then in vacuo over oil of vitriol. The tannaspidic acid thus obtained is pure if insoluble in water and ether, but completely soluble in alcohol.

*Properties.* Black-brown, amorphous, shining, friable, mass. Inodorous, with a slightly astringent taste and faint acid reaction.

a.				b.				Luck. mean. in vacuo.
26 C.....	156	....	60.46	28 C.....	168	....	60.43	.... 60.27
14 H .....	14	....	5.42	14 H .....	14	....	5.04	.... 5.65
11 O .....	88	....	34.12	12 O .....	96	....	34.53	.... 34.08
$\text{C}^{26}\text{H}^{14}\text{O}^{11}$ ....				258	....	100.00	$\text{C}^{28}\text{H}^{14}\text{O}^{12}$ ....	278 .... 100.00 .... 100.00

Luck gives the first formula; the second here proposed, agrees with the analysis of the free acid, less closely with those of the lead-salt and the derivatives. (Kr.)

*Decompositions.* 1. The clear solution of tannaspidic acid evaporated at 100°, with access of air, leaves a residue partly insoluble in alcohol. — 2. Heated in a test-tube, it gives off acid water, with an odour of burnt tartar, and leaves charcoal. — 3. Burns without residue on platinum foil. — 4. With oil of vitriol, it forms a red-brown solution, which becomes darker when heated, and is partly precipitable by water. — 5. The alcoholic acid is converted by tincture of iodine at 40° — 60°, into a brown iodated substance, which is precipitated by water, and may be freed from excess of iodine by ether free from alcohol. — 6. By dry chlorine gas, it is converted into bichlorotannaspidic acid; by moist

chlorine gas into quadrichlorotannaspidic acid, and by chlorine-water, into trichlorotannaspidic acid. — 7. The alcoholic solution, heated with hydrochloric acid, acquires a fine purple-red colour, and when mixed with water deposits a red powder. This precipitate is regarded by Luck as ethyltannaspidic acid (p. 499). A solution of tannaspidic acid in wood-spirit does not yield methyl-tannaspidic acid, when heated with hydrochloric acid. — 8. Tannaspidic acid, when heated with dilute hydrochloric acid and *chlorate of potash*, gives off a large quantity of chlorine gas, and is converted into Luck's terchloroxytannaspidic acid, which appears to be identical with terchlorotannaspidic acid. — 9. It dissolves in cold fuming *nitric acid*, without evolution of gas, forming a brown solution, precipitable by a small quantity of water. The solution yields, by evaporation, a yellow residue, not containing oxalic acid. — 10. A strong aqueous solution of *chromic acid* decomposes it with violent evolution of gas. — 11. With aqueous *potash* or *ammonia*, it forms a brown solution, which becomes darker when heated, takes up oxygen when exposed to the air, becoming purple-red or brown, and deposits brown or black flocks on addition of an acid.

Insoluble in *water*. — The alcoholic solution, mixed with ammonia, yields a brown precipitate with *chloride of barium* or *chloride of calcium*; it colours *sesquichloride of iron* green, and precipitates it on addition of ammonia. With *metallic salts*, on addition of ammonia, it forms dark-coloured precipitates, but it does not precipitate *tartar-emetic*.

*Lead-salt*. — Precipitated from the alcoholic acid by an alcoholic solution of neutral acetate of lead, and washed with weak spirit, then with water. — Black shining mass, yielding a brown powder.

<i>a.</i>				<i>b.</i>				Luck. <i>mean.</i>
26 C.....	156	...	43·21	28 C.....	168	...	44·10	43·40
13 H .....	13	...	3·60	13 H .....	13	...	3·41	3·65
10 O .....	80	...	22·16	11 O .....	88	...	23·10	22·35
PbO .....	112	...	31·03	PbO .....	112	...	29·39	30·60
<hr/>				<hr/>				
C <sup>26</sup> H <sup>13</sup> O <sup>10</sup> , PbO....	361	...	100·00	C <sup>28</sup> H <sup>13</sup> O <sup>11</sup> , PbO....	381	...	100·00	100·00

The first formula is that given by Luck.

Tannaspidic acid dissolves in *alcohol*, even in absolute alcohol. It dissolves in *acetic acid*, and is precipitated therefrom by water. It precipitates the solution of *isinglass* in aqueous alcohol.

It is insoluble in *ether*, *oil of turpentine* and *fixed oils*.

## 2. Bichlorotannaspidic Acid.

LUCK. *Jahrb. pr. Pharm.* 22, 163.

Dry chlorine gas is passed over tannaspidic acid dried in vacuo, a gentle heat being applied towards the end; the resulting hydrochloric acid is removed by dry air; the product is dissolved in alcohol, and the solution left to evaporate in contact with the air.

Amorphous cinnamon-coloured powder, having a fruity odour, a slightly acid astringent taste, and acid reaction.

								Luck. <i>In vacuo.</i>	
<i>a.</i>				<i>b.</i>					
26 C.....	156	....	47·88	28 C.....	168	....	48·41	....	47·81
11 H .....	11	....	3·37	12 H .....	12	....	3·46	....	3·35
2 Cl .....	71	....	21·74	2 Cl .....	71	....	20·46	....	21·90
11 O .....	88	....	27·01	12 O .....	96	....	27·67	....	26·94
<hr/>				<hr/>				<hr/>	
C <sup>26</sup> Cl <sup>2</sup> H <sup>11</sup> O <sup>11</sup> ....	326	....	100·00	C <sup>28</sup> Cl <sup>2</sup> H <sup>12</sup> O <sup>12</sup> ....	347	....	100·00	....	100·00

Luck gives the first formula, which does not accord with the principles of this Handbook.

The acid does not acquire a purple-colour when *heated*. It dissolves with brown colour in *potash-ley*. — With *metallic salts*, it reacts like tannaspidic acid. — Insoluble in *water*, *ether*, and *oils* both *fixed* and *volatile*, but easily soluble in *alcohol*.

### 3. Terchlorotannaspidic Acid.

LUCK. *Jahrb. pr. Pharm.* 22, 165 and 167.

#### *Trichloroxytannaspidic acid.*

*Preparation.* 1. When chlorine gas is passed into water in which tannaspidic acid is suspended, the brown acid is converted into a lighter loam-coloured powder, which may be washed, dried, dissolved in alcohol, and recovered by evaporating the alcohol. — 2. Pulverised tannaspidic acid, gently heated with hydrochloric acid and chlorate of potash, is converted, after a while, with copious evolution of chlorine, into a fiery orange-coloured powder, which separates as the liquid cools. Has an acid reaction and a sour astringent taste.

<i>a.</i>							
26 C.....	156·0	.....	41·46				
10 H .....	10·0	.....	2·65				
3 Cl .....	106·5	.....	28·23				
13 O .....	104·0	.....	27·66				
<hr/>				<hr/>			
C <sup>26</sup> Cl <sup>3</sup> H <sup>10</sup> O <sup>13</sup> .....	376·5	.....	100·00				
<i>b.</i>				Luck.			
26 C .....	156·0	.....	40·60	<i>a.</i>		<i>b.</i>	
10 H .....	10·0	.....	2·60	41·27	.....	40·39	
3 Cl .....	106·5	.....	27·64	2·69	.....	2·90	
14 O .....	112·0	.....	29·16	28·13	.....	27·33	
				27·91	.....	29·38	
<hr/>				<hr/>			
C <sup>26</sup> Cl <sup>3</sup> H <sup>10</sup> O <sup>14</sup> ....	384·5	.....	100·00	.....	100·00	.....	100·00

*a* was obtained by 1; *b* by 2; the latter is Luck's trichloroxytannaspidic acid, for which he calculates the formula *b*. The two acids appear to be identical. (Kr.)

The acid (prepared by 1) dissolves in cold, and blackens hot *oil of vitriol*.

It is insoluble in *water*, but dissolves with brown colour in aqueous *alkalis*. With *metallic salts*, it reacts like tannaspidic acid.

*Lead-salt*. — Obtained by precipitating the alcoholic solution of the acid with neutral acetate of lead. Brown flocks, forming, when dry, a black-brown shining mass.

					Luck.	
					a.	b.
26 C	156.0	...	31.94	.....	31.75	31.44
10 H	10.0	...	2.05	.....	2.11	2.18
3 Cl	106.5	...	21.80			
13 O	104.0	...	21.29			
PbO	112.0	...	22.92	.....	22.10	22.30
$C^{26}Cl^3H^{10}O^{13}, PbO$					488.5	100.00

b is the lead-salt of Luck's trichloroxytannaspidic acid =  $C^{26}Cl^3H^{10}O^{14}, PbO$ .

Tetrachlorotannaspidic acid dissolves easily in *alcohol*. The solution forms a very curdy precipitate with solution of *gelatin*. — It is insoluble in *ether* and in *oils*, both *fixed* and *volatile*.

#### 4. Quadrichlorotannaspidic Acid.

LUCK. *Jahrb. pr. Pharm.* 22, 168.

Air-dried tannaspidic acid absorbs chlorine gas with rise of temperature and evolution of hydrochloric acid gas, and forms a brown powder, which dissolves easily in aqueous *alkalis* and in *alcohol*, and gives with *metallic salts* the same reactions as tannaspidic acid.

					Luck.	
26 C	156	.....	35.61	.....	35.74	
12 H	12	.....	2.73	.....	2.81	
4 Cl	142	.....	32.33	.....	32.12	
16 O	128	.....	29.33	.....	29.33	
$C^{26}H^{12}Cl^4O^{16}$					438	100.00

#### 5. So-called Ethyl-tannaspidic Acid.

LUCK. *Jahrb. pr. Pharm.* 22, 169.

One pt. tannaspidic acid is digested in the water-bath with 14 pts. alcohol of 85 p. c. and 2 pts. hydrochloric acid of sp. gr. 1.12, for an hour or two, or till the liquid, when viewed in thin layers, exhibits a pure purple-red colour; any powder that may separate is dissolved by addition of alcohol; and the hot-filtered liquid is mixed with cold water. The light red precipitate is washed and dried.

Light purple powder, without taste or smell. Neutral.

					Luck.	
					mean; in vacuo.	
56 C	336	.....	62.81	.....	62.92	
31 H	31	.....	5.79	.....	5.79	
21 O	168	.....	31.40	.....	31.29	
$C^{56}H^{31}O^{21}$					535	100.00

So, according to Luck, who regards this compound as ethyl-tannaspidic acid,  $2C^{26}H^{13}O^{10}, C^4H^2O$ .—The body does not exhibit any of the characters of an acid ether, but appears to be related to tannaspidic acid in the same way as ledixanthin or rhodoxanthin to ledi- and rhodo-tannic acids. (Kr.)

*Decompositions.* 1. The acid turns brown when exposed to the air, more quickly at  $100^\circ$ .—2. In *alcoholic* or *ether-alcoholic* solution, it decomposes and turns brown in a few days—or more quickly at temperatures between  $60^\circ$  and  $80^\circ$ , less easily if mixed with hydrochloric acid. The brown solution recovers its original colour when treated with hydrochloric acid. In this reaction, according to Luck, the ethyl-tannaspidic acid is resolved into alcohol and tannaspidic acid, and on subsequently treating the product with alcohol [? hydrochloric acid, W.] the ethyl-tannaspidic acid is reproduced. The alcoholic solution did not however exhibit any traces of newly formed alcohol (Kr.).—3. It dissolves with orange-brown colour in *oil of vitriol*.—4. With *nitric acid*, it forms a brown-red substance.—5. The alcoholic solution is decolorised by *chlorine*.—7. By aqueous *ammonia*, or *potash-ley* of sp. gr. 1.2, it is converted into a dark-green powder; in case of greater dilution, it is dissolved, with the same colour, and when left to itself, or heated, it is converted into tannaspidic acid.

Insoluble in *water*.—When dissolved in alcohol, it forms a violet precipitate with *chloride of barium*, *calcium*, or *aluminium*, on addition of ammonia; greenish black with *ferrous chloride* and *ferric acetate*; violet-red with *protochloride of tin*; dark brown with *nitrate of silver* on addition of ammonia; dark violet with *bichloride of platinum*.

*Lead-salts.*—a. *Monobasic.* Formed by precipitating the cold alcoholic solution of the acid with neutral acetate of lead. The precipitate has a fine dark green colour, becoming dirty blue green on drying.

Calculation according to Luck.				Luck.	
56 C .....	336 .....	51.97 .....	51.99		
31 H .....	31 .....	4.79 .....	4.73		
21 O .....	168 .....	25.99 .....	26.03		
PbO .....	112 .....	17.25 .....	17.25		
<hr/>				<hr/>	
$C^{56}H^{31}O^{21}, PbO$ .....	647 .....	100.00 .....	100.00		

b. *With a larger proportion of Lead-oxide.*—Basic acetate of lead throws down from the alcoholic acid a green precipitate, soon becoming dingy green. It contains 31.08 p. c. PbO, and is therefore perhaps  $2C^{26}H^{13}O^{10}, C^4H^2O, 2PbO$  (calc. 29.43 p. c. PbO.) (Luck).

The acid dissolves in *alcohol* with dark purple colour. The solution produces a very slight turbidity in solution of *gelatin*.—The acid is insoluble in *ether*, and in *oils* both *fixed* and *volatile*.

## 6. Pteritannic Acid.

Luck. *Jahrb. pr. Pharm.* 22, 173.

See *Tannaspidic acid* (p. 496). The ethereal solution of pteritannic acid obtained as there described leaves, on evaporation, a black-brown

residue, which is digested with distilled rock-oil as long as the oil is thereby coloured brown. The undissolved powder is collected, pressed, triturated and boiled with water; the residual resinous cake is dissolved in ether; and the solution is evaporated.

Black-brown, amorphous, shining mass, yielding a fawn-coloured, electric powder. Tasteless, with a faint odour. Reacts slightly acid.

Calculation according to Luck.				Luck.	
24 C	..... 144	.....	64.57	.....	64.41
15 H	..... 15	.....	6.72	.....	6.90
8 O	..... 64	.....	28.71	.....	28.69
<hr/> C <sup>24</sup> H <sup>15</sup> O <sup>8</sup> .... 223				..... 100.00	..... 100.00

Luck's formula should be doubled to make it agree with principles of the Handbook

*Decompositions.* 1. When gently heated on platinum-foil, it melts, gives off balsamic vapours, burns with a luminous flame, and leaves charcoal. — 2. It dissolves with yellow-brown colour in oil of vitriol. — 3. Dry chlorine converts it into bichloropteritannic acid. — 4. By boiling with alcohol and hydrochloric acid, it is converted into Luck's ethylpteritannic acid (p. 503). — 5. In warm alkaline solution it absorbs oxygen, and turns brown-red.

Insoluble in Water. — The alcoholic solution forms brown precipitates with chloride of barium and chloride of calcium on addition of ammonia, and green precipitates with proto- and sesqui-chloride of iron.

*Pteritannate of Lead.* a. *Sesquibasic.* — Alcoholic pteritannic acid, mixed with excess of neutral acetate, or with basic acetate, of lead, throws down monobasic pteritannate of lead, and the liquid filtered therefrom yields, with a small quantity of ammonia, a light fawn-coloured precipitate of the sesqui-basic salt.

				Luck.	
48 C	..... 288	.....	37.32	.....	37.82
29 H	..... 29	.....	3.75	.....	3.98
15 O	..... 120	.....	15.56	.....	14.75
3 PbO	..... 336	.....	43.37	.....	43.45
<hr/> 2(C <sup>24</sup> H <sup>14</sup> O <sup>7</sup> ,PbO) + PbO,HO .... 773				..... 100.00	..... 100.00

b. *Monobasic.* Preparation just described.

				Luck.	
24 C	..... 144	.....	44.22	.....	44.07
14 H	..... 14	.....	4.30	.....	4.31
7 O	..... 56	.....	17.22	.....	17.52
PbO	..... 112	.....	34.26	.....	34.10
<hr/> C <sup>24</sup> H <sup>14</sup> O <sup>7</sup> ,PbO .... 326				..... 100.00	..... 100.00

c. *Biacid.* — By precipitating alcoholic pteritannic acid with a quantity of neutral acetate of lead, not sufficient for complete precipitation. Grey-brown precipitate.

				Luck.	
48 C	..... 288	.....	52.50	.....	52.47
29 H	..... 29	.....	5.28	.....	5.31
15 O	..... 120	.....	21.89	.....	22.12
PbO	..... 112	.....	20.33	.....	20.10
<hr/> 2C <sup>24</sup> H <sup>14</sup> O <sup>7</sup> ,PbO,HO .... 549				..... 100.00	..... 100.00



Pteritannic acid dissolves in strong *alcohol*, less freely in weak *alcohol*; easily in *ether*; but is insoluble in *oils*, both *fixed* and *volatile*.

### 7. Bichloropteritannic Acid.

LUCK. *Jahrb. pr. Pharm.* 22, 178.

Chlorine gas is passed into water containing pteritannic acid in suspension, and the product is washed, dried, and purified by solution in *ether*.

Light loam-coloured powder, tasteless, but with a slight fruity smell.

Calculation according to Luck.				Luck.
24 C .....	144	.....	47·87	..... 47·54
14 H .....	14	.....	4·65	..... 4·80
2 Cl .....	71	.....	23·54	..... 23·33
9 O .....	72	.....	23·94	..... 24·33
<hr/>				
$C^{24}H^{14}Cl^2O^8, HO$ .....	301	.....	100·00	..... 100·00

Insoluble in *water*. — Reacts with *metallic-salts* like terchloropteritannic acid.

*Lead-salts*. — By precipitating the alcoholic acid with neutral acetate of lead, precipitates are formed, containing from 5 to 15 p. c.  $PbO$ . — The *monobasic* salt is obtained by precipitating the alcoholic acid with basic acetate of lead.

				Luck.
24 C .....	144	.....	35·70	..... 35·85
13 H .....	13	.....	3·22	..... 3·23
2 Cl .....	71	.....	17·58	
8 O .....	64	.....	15·84	
$PbO$ .....	112	.....	27·66	..... 27·63
<hr/>				
$C^{24}H^{13}Cl^2O^8, PbO$ .....	404	.....	100·00	

Bichloropteritannic acid dissolves in *alcohol* and *ether*, but is insoluble in *oils*, both *fixed* and *volatile*.

### 8. Terchloropteritannic Acid.

LUCK. *Jahrb. pr. Pharm.* 22, 177.

Dry chlorine gas is passed over dry pteritannic acid; the resulting hydrochloric acid is expelled by dry air, and the product is purified by solution in *alcohol*.

Orange-coloured powder, having a faint peculiar odour, a scarcely bitter taste, and an acid reaction.

Calculation according to Luck.				Luck.
24 C	144.0	44.14	44.13	
12 H	12.0	3.67	3.91	
3 Cl	106.5	19.63	19.77	
8 O	64.0	32.56	32.19	
$C^{24}H^{12}Cl^3O^8$				
	326.5	100.00	100.00	

When heated on platinum-foil, it melts and gives off acid vapours.

It is insoluble in water.—It dissolves with brown colour in aqueous *alkalis*.—The alcoholic solution forms a green precipitate with *proto- and sesqui-chloride of iron*, light brown with *chloride of copper*, no precipitate with *chloride of calcium* or *barium*, *nitrate of silver*, or *tar-tar-emetic*.

*Lead-salt*.—From an alcoholic solution of terchloropteritannic acid, basic acetate of lead throws down a precipitate which contains 25.27 p. c. PbO, and is, therefore,  $C^{24}H^{12}Cl^3O^8, PbO$  (calc. 25.48 PbO).

The acid dissolves readily in *alcohol* and *ether*, but is insoluble in *oils*, both *fixed* and *volatile*. It forms a slight precipitate with *gelatin-solution*.

## 9. So-called Ethyl-pteritannic Acid.

LUCK. *Jahrb. pr. Pharm.* 22, 179.

A solution of pteritannic acid in absolute alcohol is boiled with a small quantity of hydrochloric acid, and the purple-red solution is (a) either dropt, with stirring, into a large quantity of water, or (b) mixed with a small quantity of water.

Prepared by a: Light purple-violet powder; by b: Black-red resin, yielding a dark-red powder. Tasteless, with scarcely acid reaction.

Calculation according to Luck.				Luck.	
a.	b.			a.	b.
52 C	65.82	52 C	67.09	65.74	67.03
34 H	7.17	33 H	7.09	7.22	7.05
16 O	27.01	15 O	25.82	27.04	25.92
$C^{52}H^{34}O^{16}$					
	100.00	$C^{52}H^{33}O^{15}$	100.00	100.00	100.00

Luck splits the formula a into  $2C^{24}H^{14}O^7, C^4H^5O, HO$ ; b into  $2C^{23}H^{14}O^7, C^4H^5O$ .—Till the resolution of the so-called ethyl-pteritannic acid into pteritannic acid and alcohol is established by experiment, this body may be more probably regarded as a compound analogous to ledixanthin (p. 528) and rhodoxanthin. (Kr.)

When dissolved in *alcohol*, it decomposes, with formation of pteritannic acid, less easily when mixed with hydrochloric acid.—It is decomposed by *chlorine* or by *nitric acid*.—Its solution in aqueous *ammonia* or *potash* turns brown on standing.

The acid is insoluble in *water*, but dissolves with brown colour in *oil of vitriol*, and is precipitated therefrom by water.—It dissolves with green colour in aqueous *alkalis*.—The alcoholic solution mixed with a little ammonia forms a green precipitate with *chloride of barium* or *calcium*, bluish violet with *chloride of aluminium*, blackish green with *proto- or sesqui-chloride of iron*. It precipitates *cupric acetate* violet.

Colours *proto-chloride of tin* violet, and on addition of ammonia, precipitates it bluish green.

*Lead-salt.* The alcoholic solution of the acid forms with neutral and basic acetate of lead, green precipitates which become violet-grey when dry. The precipitate, formed with an insufficient quantity of the neutral acetate contains 10.5 p. c.  $PbO$ ; that formed with excess of the neutral acetate or with an insufficient quantity of basic acetate, contains 21.55 p. c.; and that formed with excess of the basic acetate, contains 33.59 p. c.  $PbO$ .

Ethyl-pteritannic acid dissolves easily in *alcohol* and in *ether*, forming purple solutions. It produces but slight turbidity in solution of *gelatin*.

### E.—Caffetannic and Viridic Acids.

#### Caffetannic Acid.



PFÄFF. *Schw.* 62, 31.

BOLLE. *N. Br. Arch.* 25, 271.

ROCHLEDER. *Ann. Pharm.* 59, 300. — *Ann. Pharm.* 63, 193; abstr. *Pharm. Centr.* 1847, 913. — *Wien. Akad. Ber.* 1, 224; *Ann. Pharm.* 66, 35; *Pharm. Centr.* 1848, 697; *Wien. Akad. Ber.* 1, 228; *Ann. Pharm.* 66, 39; *Pharm. Centr.* 1848, 701. — *Wien. Akad. Ber.* 7, 815; *J. pr. Chem.* 56, 93; *Ann. Pharm.* 82, 194; *Pharm. Centr.* 1852, 364. — *Wien. Akad. Ber.* 24, 39; *J. pr. Chem.* 72, 392; *Chem. Centr.* 1858, 75.

PAYEN. *Compt. rend.* 22, 724; 23, 8, and 244; *N. Ann. Chim. Phys.* 26, 108; *J. pr. Chem.* 38, 471.

ROCHLEDER & HLASIWETZ. *Wien. Akad. Ber.* 5, 6; *J. pr. Chem.* 51, 415; *Ann. Pharm.* 76, 338; *Chem. Gaz.* 1851, 121.

*Caffeic acid* (Rochleder). Discovered by Pfaff. The latter, on precipitating the aqueous decoction of coffee-beans with neutral acetate of lead, and decomposing the precipitate under water with hydrosulphuric acid, and evaporating the filtrate to a syrup, found that it separated into a soluble portion containing caffetannic acid, and an insoluble portion containing *aromatic caffeic acid*. Bolle and Rochleder were unable to find the latter. — With caffetannic acid we shall here place, as Rochleder does, Payen's chlorogenic acid separated from the *Sel naturel du café*, or chlorogenate of caffeine and potash, whereas Zwenger & Siebert (*Ann. Pharm. Suppl.* 1, 77) regard that salt as identical with the kinic acid which they found in coffee. Against the latter view must be alleged, amongst other statements of Payen, that his *Sel naturel* contains nitrogen.

*Occurrence.* In the beans and leaves of the coffee-tree (*Handb.* viii, *Phytochem.* 55), in the leaves of *Ilex paraguayensis* (*ibid.* 22), and in the root of *Chiococca ramosa* (*ibid.* 56).

Runge's *Verdic acid* (*Grunssäure*). — In the root-stock of *Scabiosa succisa*, as well as in many *Compositæ* (*Handb.* viii, *Phytochem.* 70) in *Synantharææ* (*ibid.* 65) and in *Umbelliferaæ*, there is found an acid, forming, with ammonia, a yellow compound, which turns blue-green in contact with the air. This verdic acid is, according to Runge,

characteristic of the above-mentioned tribes of plants; it exhibits some points of resemblance to valerotannic acid (p. 533), also to caffetannic acid and rubichloric acid (see *Rubian*). — The root-stock of *Scabiosa succisa*, after being cleansed, pulverised, and dried, is exhausted with alcohol; the solution is precipitated with ether; the white precipitate is collected and washed with ether, and its aqueous solution is precipitated with neutral acetate of lead. On decomposing the precipitate under water with hydrosulphuric acid, and evaporating the filtrate, the verdic acid remains as an amorphous, yellow, brittle, and acid mass. The aqueous solution of this verdic acid, if exposed to the air without being mixed with ammonia, does not undergo any alteration, but if ammonia is present, the solution takes up oxygen and turns green; the same effect is produced, in a less degree in presence of potash or soda. The green compound thus formed, is decolorised by contact with zinc-amalgam, and becomes green again by contact with the air. From the green solution, acids throw down a red-brown precipitate, which dissolves with green colour in the fixed alkalis and in ammonia. — The salts of the alkaline earths and heavy metallic oxides form white precipitates with colourless verdic acid, dark green precipitates with the green variety. Neutral acetate of lead precipitates the former yellow, the latter blackish green; this last mentioned lead-salt contains more oxygen than the yellow.

*Preparation of Caffetannic Acid.* — Coffee-beans dried at 60° and pulverised are exhausted with ether, which takes up fat, caffeine, and a small quantity of caffetannic acid; the residual powder is boiled with alcohol of 40 per cent.; the filtrate is mixed with twice its own bulk of water; the precipitated fat-flocks are separated; the liquid is boiled; solution of neutral acetate of lead is added to it; and the whole is boiled for a few seconds, which causes the precipitate to contract, and renders it easier to filter. The precipitate is washed with water containing alcohol, decomposed under water with hydrosulphuric acid, and the pale yellow filtrate is evaporated over the water-bath (Rochleder). — When the decoction of coffee-beans is mixed in separate portions with neutral acetate of lead, the precipitate first formed contains citric acid, the latter only caffetannic acid. When the aqueous decoction is completely precipitated with neutral acetate of lead, the precipitate decomposed with hydrosulphuric acid, and the filtrate evaporated to a syrup, a mixture of caffetannic acid, with its salts and citric acid, is obtained, which yields, with neutral acetate of lead, a lemon-yellow precipitate, containing acetic acid. An impure lead-salt of this kind is described in *Ann. Pharm.* 63, 200 (Rochleder).

See also the preparation of viridic acid (p. 510), and that of the lead-salts (p. 510).

When Payen's chlorogenate of caffeine and potash (p. 509) is decomposed by an equivalent quantity of sulphuric acid, and the solution mixed with pounded marble and evaporated to dryness, alcohol extracts from the residue acid chlorogenate of caffeine, the acid of which may be precipitated by basic acetate of lead. In like manner, by precipitating the alcoholic solution of chlorogenate of caffeine and potash with basic acetate of lead, or by triturating the salt with water and oxide of lead, chlorogenate of lead is obtained, which, in the latter case, is retained in solution by help of the potash, and may be precipi-

tated by passing carbonic acid into the liquid. The washed lead-salt, decomposed by hydrosulphuric acid, yields aqueous chlorogenic acid, which, by rapid evaporation, may be obtained as a confused crystalline mass. This acid is white; separates from its aqueous solution by slow evaporation in microscopic prisms, containing 56.0 p. c. C., 5.6 H., and 38.4 O., agreeing with the formula  $C^{14}H^6O^7$  (calc 56.7 p. c. C., and 5.4 H.); and has a strong acid reaction. When heated, it melts, turns yellow, chars, and gives off a brown liquid. Its lead-salt contains 60 p. c. lead-oxide. It is more soluble in aqueous than in absolute alcohol.

*Properties of Caffetannic Acid.*—Brittle mass, which may be rubbed to a yellowish white powder; has a slightly sour and somewhat astringent taste (Rochleder).

at 100°.				Rochleder.
				mean.
14 C .....	84 .....	56.75 .....		56.53
8 H .....	8 .....	5.41 .....		5.54
7 O .....	56 .....	37.84 .....		37.93
<hr/>				
$C^{14}H^6O^7$ .....	148 .....	100.00 .....		100.00

Rochleder formerly gave the formula  $C^{16}H^8O^8$ , which requires nearly the same numbers. — For Laurent's formula, see *Compt. rend.* 35, 161.

*Decompositions.* 1. When caffetannic acid is subjected to *dry distillation*, the melting mass swells up, and gives off, first water, then a yellowish viscid distillate, smelling like carbolic acid, together with oil-drops, and leaves charcoal. The viscid distillate, collected apart, solidifies to a crystalline mass of pyrocatechin. The acid heated on platinum foil gives off an unpleasant odour of acetic acid, burns with a bright flame, and leaves a residue of charcoal. Heated in a glass tube, it emits the odour of burnt coffee (Rochleder).—2. The solution in *oil of vitriol* assumes a blood-red colour when heated, and is decolorised and precipitated by water. When aqueous caffetannic acid is boiled for several hours with dilute sulphuric acid, it is partially oxidised to viridic acid (p. 510), but remains for the most part unaltered.—3. *Nitric acid* produces in the concentrated aqueous solution a violent evolution of gas; dilute nitric acid forms prussic acid and a large quantity of oxalic acid, but no peculiar acid (Rochleder).

4. On mixing caffetannic acid with a concentrated aqueous solution of *bichromate of potash*, the liquid acquires a darker colour, and deposits flocks, an additional quantity of which is thrown down by acetic acid.—These flocks, after drying in vacuo, contain 33.34 p. c. C., 4.27 H., 41.61 O., and 20.78  $Cr^2O^3$  (or a quantity of chromic acid equivalent to this quantity of chromic oxide) corresponding to the formula  $C^{12}H^4O^{38}, 2Cr^2O^3$  (Rochleder & Payr.).

5. In contact with aqueous *ammonia*, caffetannic acid absorbs *oxygen*, and is converted into viridic acid (p. 510). Carbonic acid is produced at the same time (Rochleder).—6. Caffetannic acid, mixed with *potash-ley*, assumes a brown colour in contact with the *air*. Alcohol precipitates the resulting potash-salt, partly as a resin, partly as a syrup, which dissolves in water, after the slightly coloured spirit has

been poured off. From this solution, after it has been neutralised with acetic acid, neutral acetate of lead throws down a brown precipitate, whereas a green precipitate is produced if the solution has been previously boiled (Rochleder). When a moderately concentrated aqueous solution of caffetannic acid is mixed with potash-ley till it exhibits an alkaline reaction, and left for a week in contact with the air, the liquid, which is brown after the potash has been added, acquires a darker colour, and becomes opaque. The light brown salt, then precipitated by neutral acetate of lead, after neutralisation with acetic acid, contains, on the average, 28.60 p. c. C., 2.08 H., 18.10 O., and 51.22 PbO., as required by the formula  $4(C^{12}H^8O^6, PbO) + 2 C^{17}H^6O^5, 3PbO$ . If the remainder of the alkaline liquid be exposed to the air for another 8 days, the lead-precipitate obtained from it is dark brown, and contains, on the average, 21.33 p. c. C., 1.51 H., 16.82 O., and 60.34 PbO. The latter precipitate is regarded by Liebig as a mixture of a basic and a neutral salt of an acid containing  $C^{12}H^4O^7$ , according to the formula  $5(C^{12}H^4O^7, 2PbO) + C^{12}H^4O^7, PbO$  (G. Liebig, *Ann. Pharm.* 71, 57).—6. The aqueous solution of caffetannic acid exposed to the air, in contact with *bicarbonate of lime*, yields viridic acid, and a black product insoluble in acid water, which forms a dark violet compound with lime (Rochleder).—7. From a moderately dilute solution of *nitrate of silver*, it throws down a precipitate from which metallic silver separates on heating or standing (Rochleder).

*Combinations.* Caffetannic acid dissolves readily in *water*, and is not precipitated by alcohol even from the syrupy solution. It dissolves in *oil of vitriol*.

Caffetannic acid dissolves in aqueous *ammonia*, with yellow colour, and in strong *potash-ley*, with reddish yellow colour, becoming pale yellow when the liquid is heated. Its compounds with baryta and lime are yellow, and quickly turn green on exposure to the air, unless the acid is in excess (Rochleder. *vid. sup.*).

*Baryta-salt.*—Concentrated aqueous caffetannic acid is neutralised with the necessary quantity of baryta-water; an equal quantity of caffetannic acid is added (since the neutral salt would decompose); the solution is evaporated over the water-bath, and alcohol added by small portions towards the end of the process. As soon as the evaporation has been carried so far that a drop of the liquid placed upon a cold glass plate becomes milk-white, or throws out resinous flocks, the solution is strained through linen into a warmed glass, a few flocks then remaining. The filtrate, on cooling, solidifies to a transparent colourless jelly, which is to be pressed between linen and paper, and dried at  $100^{\circ}$ . Faintly greyish yellow, earthy mass, containing 46.29 p. c. C., 4.57 H., 30.69 O., and 18.45 BaO (Rochleder).

When baryta-water in excess is added to aqueous caffetannic acid, a pale yellow precipitate is formed if the excess of baryta is small, but with a larger excess, an orange-yellow precipitate is formed, which turns green and brown on the filter.

*Lead-salts.*—The lead-salts of caffetannic acid do not oxidise so readily in contact with the air; nevertheless they exhibit a variable constitution, and cannot be heated above  $100^{\circ}$  without change (Rochleder).

a. When the alcoholic decoction of coffee-beans, after being freed from fat, is heated to the boiling point, and precipitated with solution of neutral acetate of lead, the resulting yellow precipitate, washed with alcohol and dried at  $100^{\circ}$ , contains 25.28 p. c. C., 2.29 H., 13.73 O., and 58.70 PbO (Rochleder).

b. When a boiling aqueous solution of neutral acetate of lead is precipitated by pouring a decoction of coffee-beans into it by small portions, a pale yellow gummy precipitate is formed, which, after washing with alcohol and drying at  $100^{\circ}$ , contains 24.73 p. c. C., 2.41 H., 15.49 O., and 57.37 PbO (Rochleder).

c. From a concentrated aqueous solution of caffetannic acid, aqueous neutral acetate of lead throws down at first a white precipitate, which becomes yellow when more acetate of lead is added. The first precipitate melts at  $100^{\circ}$  to a green oil, which then solidifies to a brittle resin, and contains 7 at. acid (according to Rochleder's older formula  $C^{16}H^8O_7$ ) to 4 at. lead oxide. The yellow precipitate contains 42.44 p. c. C., and 4.16 H. — By precipitating concentrated aqueous caffetannic acid with neutral acetate of lead, another salt was once obtained, containing 35.34 p. c. C., and 40.25 PbO. — Another lead-salt accidentally formed, contained, at  $100^{\circ}$ , 29.88 p. c. C., 2.43 H., 16.15 O., and 51.54 PbO. (Rochleder.)

d. When dried coffee-beans are boiled with alcohol of  $40^{\circ}$ , the filtrate, while still hot, precipitated with neutral acetate of lead, the precipitate washed with alcohol, and decomposed under alcohol with hydrosulphuric acid, and the filtrate, after being freed from hydrosulphuric acid, poured into an excess of alcoholic neutral acetate of lead, the resulting precipitate dried at  $100^{\circ}$ , contains 25.00 p. c. C., 2.4 H., 16.89 O., and 85.87 PbO., answering to the formula  $C^{42}H^{24}O^{21}, 5PbO$ , or  $3C^{14}H^8O_7, 5PbO$ . (Rochleder.)

e. When an extract of coffee-beans, prepared with cold aqueous alcohol is precipitated with neutral acetate of lead, the precipitate decomposed under water by hydrosulphuric acid, the filtrate evaporated to a syrup, this syrup precipitated with absolute alcohol and filtered, the filtrate evaporated, and the residue dissolved in water, and freed from fat by addition of a few drops of neutral acetate of lead, — the filtrate, poured into an excess of aqueous neutral acetate of lead, forms a precipitate which, after washing with cold water, becomes greenish at  $100^{\circ}$ . This precipitate contains, on the average, 28.32 p. c. C., 2.58 H., 19.01 O., and 50.09 PbO., and is, therefore,  $C^{42}H^{24}O^{21}, 4PbO$  or  $3C^{14}H^8O_7, 4PbO$ . (Rochleder.)

f. From the alcoholic decoction of the bark of cainca-root, alcoholic neutral acetate of lead throws down a precipitate which contains small quantities of caincin and mineral acids, and when decomposed by hydrosulphuric acid, and several times fractionally precipitated by neutral acetate of lead, yields caffetannate of lead containing 40.83 p. c. C., 4.11 H., 29.40 O., and 25.66 p. c. PbO. (Rochleder & Hlasiwetz, *Wien. Akad. Ber.* 5, 6.)

g. The lead-salt of caffetannic acid from *Ilex paraguayensis* contains 22.84 p. c. C., 2.20 H., 19.64 O., and 59.32 PbO., answering to the formula  $C^{14}H^8O_7, 2PbO$ . It is obtained by exhausting the bruised herb with alcohol of  $40^{\circ}$ , mixing the filtrate with alcoholic neutral acetate of lead, removing the precipitate as long as it does not exhibit a pure yellow colour, and completely precipitating the filtrate. The last precipitate is washed with alcohol, and decomposed under alcohol

with hydrosulphuric acid; the filtrate, after being freed from sulphide of lead and excess of hydrosulphuric acid, is reprecipitated with alcoholic neutral acetate of lead; and the precipitate is washed with alcohol and dried at 100°. (Rochleder.)

Aqueous caffetannic acid does not precipitate *ferrous sulphate*, but on addition of ammonia, an almost black precipitate is formed, which dissolves in acetic acid with bottle-green colour. The precipitate contains variable quantities of protoxide of iron; the carbon and hydrogen are in the same proportion as in free caffetannic acid. (Rochleder.) Aqueous caffetannic acid forms a dark-green precipitate with *ferric chloride*.

*Caffetannate of Copper* is obtained from an acid solution as a grey salt of variable composition, which, so long as it remains moist, melts at 100° to a green resin, and dissolves with green colour in water containing a little ammonia, with blue colour when more ammonia is present. The basic copper-salts are green. (Rochleder.)

Caffetannic acid dissolves in all proportions in *alcohol*, even when absolute.

*Chlorogenate of Caffeine and Potash*.—See page 504. — When coffee powder exhausted with ether is treated with alcohol of 60 p. c., the solution evaporated to a syrup, and this syrup mixed with three times its volume of alcohol of 85 p. c., the liquid separates into two layers, the upper, which is mobile, containing the greater part of the chlorogenate of caffeine and potash. The remaining quantity of this salt may be obtained by dissolving the lower viscid layer in a small quantity of water, mixing it with alcohol, and pouring off the alcoholic solution. The united alcoholic solutions are evaporated to a syrup; this syrup is mixed with a little alcohol, and left to crystallise; and the product is purified by washing and recrystallisation from weak spirit.

Radiate prisms, united in spheroidal groups. The salt dried at 100° becomes electric by trituration on the still warm paper, and attaches itself in long flakes to a knife held above it. — It contains 50.74 p. c. C., 5.38 H., 9.12 N., and 7.50 KO., or 63.5 chlorogenic acid, 29.0 caffeine, and 7.5 potash. — It does not change at 150°, but melts at 185° to a yellow mass, which swells up to five times its original volume, but remains solid and friable. At 200° it decomposes, turns brown, and gives off vapours which condense to crystals of caffeine; when further heated, it melts again, gives off a large quantity of ammonia, swells up to twenty times its original bulk, and leaves a very light iridescent charcoal. The aqueous solution, when exposed to the air, turns yellow and afterwards greenish-brown. It is not altered by nitrate of silver, but becomes yellowish-brown on addition of a small quantity of ammonia. The mixture, after standing for some time, becomes turbid from separation of metallic silver. When the aqueous solution is mixed with a few drops of ammonia, and exposed to the air in a shallow dish, the water and ammonia being frequently renewed, it assumes, in the course of 24 hours, first a yellow, then a green and blue-green, and ultimately a brown colour. If it be evaporated to dryness after 20 or 30 days, anhydrous alcohol extracts caffeine from the dark brown residue. — Oil of vitriol, heated



with the salt, colours it dark violet; hydrochloric acid acts in a similar manner, whereas nitric acid produces an orange-yellow coloration. The crystals, gently heated with lumps of potash, assume a scarlet or orange-red colour; and at a stronger heat, the mass melts, turns brown, gives off a large quantity of ammonia, and decomposes.—On the preparation of chlorogenic acid from chlorogenate of caffeine and potash, see page 505.

Chlorogenate of caffeine and potash is very soluble in water, the the hot saturated solution solidifies on cooling. For the decompositions of the aqueous solution, see page 509.—It forms a greenish-yellow precipitate with neutral acetate of lead, and from the basic acetate it throws down flocks of a pure yellow colour.—In absolute alcohol it is nearly insoluble even when heated; in ordinary alcohol it dissolves more abundantly as the proportion of water is greater, and crystallises from the solution on cooling. (Payen.)

### Viridic Acid.

ROCHLEDER. *Ann. Pharm.* 63, 193.—*Wien. Akad. Ber.* 1, 227; *Ann. Pharm.* 66, 38.

Produced from caffetannic acid by oxidation in presence of aqueous ammonia (p. 506) (Rochleder); under the same influences from quinovatannic acid (p. 485) (Elsawetz).

*Preparation.*—1. When the alcoholic decoction of dried and pulverised coffee-beans is mixed with water to separate fat, the filtrate heated to the boiling point with neutral acetate of lead, and the precipitate decomposed under water with hydrosulphuric acid, aqueous caffetannic acid is obtained, which, when supersaturated with ammonia, assumes a colour varying from dark yellow to red brown, and changing in contact with the air to greenish yellow, and after 36 hours, to blue-green. To prepare viridic acid, the blue-green liquid is mixed with excess of acetic acid, then with alcohol, which throws down black flocks, of a compound similar to metagallic acid, which is formed at the same time [but not necessarily, according to Rochleder (*Wien. Akad. Ber.* 1, 227),]—the liquid is then filtered, and the brown filtrate precipitated with neutral acetate of lead.—2. When the aqueous extract of coffee-beans, previously exhausted with alcohol, is precipitated at the boiling heat with neutral acetate of lead,—the yellow precipitate decomposed under alcohol with hydrosulphuric acid, and the filtrate, after being freed from excess of hydrosulphuric acid, supersaturated with ammonia, exposed to the air for 24 hours—and then mixed with 2 vol. alcohol of 40°, a greenish-blue precipitate is formed, which, when washed with alcohol containing acetic acid, then dissolved in acetic acid and precipitated with neutral acetate of lead, yields viridate of lead.

By decomposing the lead-salt with aqueous hydrosulphuric acid, and removing the sulphide of lead, aqueous viridic acid is obtained as a brown liquid, which, when evaporated, leaves a brown amorphous mass. This substance dissolves easily in water, with fine carmine colour in oil of vitriol, and is precipitated therefrom in blue flocks by water.

Aqueous viridic acid assumes a dark green colour when mixed with ammonia, potash or soda. Baryta-water precipitates it in blue-green flocks, which, after washing with alcohol and drying at 100°, contain 43·15 p. c., baryta, as required by the formula  $C^{14}H^8O^9, 2BaO$  (calc. 43·46 p. c. BaO).

*Lead-salt.* — For the preparation, page 510. Green-blue or indigo-blue precipitate.

<i>a.</i> at 100°.			Rochleder.	<i>b.</i> at 100°.			Rochleder.
14 C	.....	32·61	.... 31·77	14 C	.....	31·51	.... 31·37
6 H	.....	2·33	.... 2·33	7 H	.....	2·63	.... 2·81
7 O	.....	21·75	.... 21·15	8 O	.....	24·01	.... 23·95
PbO	.....	43·31	.... 44·75	PbO	.....	41·85	.... 41·87
$C^{14}H^6O^7, PbO$ ....			100·00 .... 100·00	$C^{14}H^7O^8, PbO$ ....			100·00 .... 100·00

*a.*, prepared by 1; *b.*, by 2.

*Cuprous Viridate.* — From the mixed solutions of cupric acetate and quinovatannic acid (p. 485), alcohol throws down dirty green flocks, which dissolve in boiling water: potash added to the cooled solution throws down cuprous hydrate. These green flocks consist of cuprous viridate (Hlasiwetz, *Wien. Akad. Ber.* 6, 271).

at 100°.			Hlasiwetz.		
56 C	.....	336	.... 45·07	.....	44·73
34 H	.....	34	.... 4·56	.....	4·77
39 O	.....	312	.... 41·86	.....	41·83
2 Cu	.....	64	.... 8·51	.....	8·67
$4C^{14}H^8O^6, Cu^2O + 2aq.$ ....			746	.... 100·00	..... 100·00

Hlasiwetz examined also another copper-salt, the composition of which approximated to the formula  $2C^{14}H^8O^9, Cu^2O, HO$ .

## F.—Isolated Tannic Acids (arranged Alphabetically).

### 1. Anacahuitta-tannic Acid.

L. MÜLLER. *Pharm. Viertelj.* 10, 519.

Found in anacahuitta-wood, a Mexican drug. — It is obtained as a lead-salt from the decoction of the wood or the bark, by precipitation with neutral acetate of lead, and purified by dissolving it in acetic acid, and precipitating the filtrate with ammonia. The lead-salt dried at 100°, contains, on the average, 18·72 p. c. carbon, 2·41 hydrogen, 15·70 oxygen, and 63·17 protoxide of lead, answering to the formula  $C^{18}H^{12}O^{10}, 3PbO$ . — The aqueous solution of the tannic acid, separated from the lead-salt by hydrosulphuric acid, has a rough and somewhat bitter taste, forms a greenish black precipitate with ferric chloride, and brown with solution of gelatin.

## 2. Aspertannic Acid.



R. SCHWARZ. *Wien. Akad. Ber.* 6, 446; *J. pr. Chem.* 55, 398; abstr. *Ann. Pharm.* 80, 334; *Pharm. Centr.* 1851, 929; *Chem. Gaz.* 1852, 61; *Lieb. Kopp. Jahresber.* 1851, 417.

*Occurrence.* In the herb of *Asperula odorata* (Schwarz).—According to Vielguth (who, however, did not compare the true aspertannic acid with that which he obtained), it occurs also in the herb of *Galium Mollugo* (see below).

*Preparation.* 1. The alcoholic extract of the herb is distilled to expel the alcohol; the residue is mixed with water; the filtrate precipitated with neutral acetate of lead; the washed precipitate is dissolved in dilute acetic acid; the filtered solution is mixed with absolute alcohol till grey flocks are precipitated; these are removed; and the filtrate is completely precipitated with absolute alcohol: the precipitate consists of the lead-salt *a*.—If the filtrate be precipitated with basic acetate of lead,—the precipitate washed with alcohol, decomposed with hydrosulphuric acid and alcohol, and the solution, freed from sulphide of lead and hydrosulphuric acid, be mixed with neutral acetate of lead,—a precipitate is obtained, consisting of the salt *b*.—2. The aqueous decoction of the herb is precipitated with neutral acetate of lead, the washed precipitate is dissolved in acetic acid; and the salt *c* is precipitated partly from the solution by basic acetate of lead, partly from the liquid filtered therefrom, by the neutral acetate.

The acid is separated from the lead-salts by decomposing them with hydrosulphuric acid, and evaporating the filtrate in a stream of carbonic acid.

*Properties.* Inodorous mass, having a faint brown colour. Very hygroscopic.

	at 100°.		R. Schwarz.	
14 C .....	84	.....	50.90	..... 51.08
9 H .....	9	.....	5.43	..... 5.19
9 O .....	72	.....	43.65	..... 43.73
<hr/>				
$C^{14}H^{20}O^8.HO$	165	.....	100.00	..... 100.00

So according to Schwarz.—According to Laurent, it is perhaps  $C^{40}H^{20}O^{26} = 2C^{14}H^{10}O^{10}$  (rubichloric acid) +  $C^{12}H^{12}O^{12} - 6HO$  (*Compt. rend.* 35, 161).

*Decompositions.* When the acid, neutralised with potash and thereby coloured brown-red, is exposed to the air, it takes up oxygen, becomes darker, and ultimately black-brown and opaque. If then mixed with acetic acid and neutral acetate of lead, separated by filtration from the slight red-brown precipitate thereby formed, and further precipitated with basic acetate of lead, it yields a red-grey lead-salt, which, after washing with alcohol and drying at 100°, con-

tains 8.69 p. c. C., 0.83 H., 8.18 O., and 82PbO, therefore, according to Schwarz, =  $C^{36}H^{20}O^{26}, 18PbO$  or =  $3C^{12}H^6O^8, 5H_2O, 18PbO$ . — The green solution of *cupric carbonate* in aqueous aspertannic acid forms, with alcohol, a green precipitate, which, after washing with alcohol and drying at  $100^\circ$ , contains 33.98 p. c. cuprous oxide, and after deduction of this, 38.88 p. c. C., 5.43 H., and 55.69 O.: hence Schwarz supposes that the oxidised tannic acid in the green precipitate =  $C^{14}H^7O^{10}, 5H_2O$  (calc. 38.88 C., 5.55 H., and 55.57 O.). — *Nitrate of silver* oxidises aspertannic acid, with separation of metallic silver. — Aspertannic acid is decomposed by boiling with dilute *hydrochloric* or *sulphuric acid*. If the neutralised solution be boiled till it no longer alters the colour of ferric chloride, the whole of the sulphuric acid then precipitated with basic acetate of lead, and more of that reagent added to the filtrate, a light yellow precipitate is formed, which, when washed with alcohol and dried at  $100^\circ$ , contains 23.06 p. c., C., 1.48 H., 10.52 O., and 64.94 PbO., and, according to Schwarz, may be represented by the formula  $C^{60}H^{21}O^{21}, 9PbO$  or  $5C^{12}H^4O^4, 9H_2O, 9PbO$  (calc. 23.11 C., 1.34 H., 10.91 O., and 64.64 PbO).

Aspertannic acid dissolves very easily in *water*. — It does not precipitate *tartar-emetic*.

*Aspertannate of Lead*. — Preparation, see above. The salts must be dried at  $100^\circ$ , at which temperature they do not turn green.

a.				b.							
56 C	.....	25.79	.....	25.85	28 C	.....	26.34	.....	26.23		
33 H	.....	2.53	.....	2.50	15 H	.....	2.35	.....	2.48		
33 O	.....	20.29	.....	20.68	15 O	.....	18.83	.....	18.90		
6 PbO	....	51.39	.....	50.97	3 PbO	....	52.48	.....	52.39		
100.00				.....	100.00	100.00				.....	100.00
c.				Schwarz.							
56 C	.....	20.86	.....	20.69	30 H	.....	1.86	.....	1.83		
30 H	.....	1.86	.....	1.83	30 O	.....	14.99	.....	15.47		
30 O	.....	14.99	.....	15.47	9 PbO	.....	62.29	.....	62.01		
9 PbO	.....	62.29	.....	62.01							
100.00				.....	100.00						

Schwarz resolves these formulæ as follows: *a* into  $4C^{14}H^8O^8, 6PbO + aq.$ ; *b* into  $2C^{14}H^7O^7, 3PbO + aq.$ ; *c* into  $4C^{14}H^7O^7, 3PbO + 2aq.$

Aspertannic acid forms a dark green precipitate with aqueous *ferric chloride*. — It is insoluble in *alcohol*, sparingly soluble in *ether*, and does not precipitate *white of egg* or *solution of gelatin*.

*Aspertannic Acid from Galium Mollugo*. — Obtained as a lead-salt from the aqueous decoction of the herb, by precipitating with neutral acetate of lead, dissolving the precipitate in acetic acid, and precipitating the filtrate with ammonia. — The acid separated from the lead-salt by hydrosulphuric acid has a slight brownish yellow colour, is inodorous, and has a slightly sour, astringent taste. It precipitates *ferric chloride* dark green, and is but partially precipitated by *neutral acetate of lead*; completely by the *basic acetate*. — The lead-salt, dried at  $110^\circ$ , contains, on the average, 21.71 p. c. C., 2.23 H., 17.93 O., and 58.13 PbO, answering to the formula  $4PbO, 2C^{14}H^8O^8, 11O$  (calc. 21.89 C., 2.21 H., 17.72 O., and 58.18 PbO). (Vielguth, *Pharm. Viertelj.* 5, 193).

## 3. Atherospermatannic Acid.

ZEYER. *Pharm. Viertelj.* 10, 511.

In the bark of *Atherosperma moschatum*, a South American drug. — The decoction of the bark clarified by several days' rest is precipitated with neutral acetate of lead, the washed precipitate is dissolved in acetic acid, and the filtrate is precipitated by ammonia. The lead-salt thus prepared, and dried at  $100^{\circ}$ , contains, on the average, 31.39 p. c. C., 3.67 H., 8.05 O., and 56.89 PbO., answering to the formula  $C^{20}H^{14}O^4, 2PbO$ . If the dirty yellow precipitate formed in the aqueous extract of the bark by neutral acetate of lead be decomposed under water by hydro-sulphuric acid, the light yellow filtrate exhibits an acid reaction, tastes slightly astringent, turns ferric chloride green, and is precipitated in flocks by excess of lime-water.

## 4. Callutannic Acid.



ROCHLEDER. *Wien. Akad. Ber.* 9, 286; *J. pr. Chem.* 58, 189; *Ann. Pharm.* 84, 354; *Pharm. Centr.* 1852, 756; *Chem. Gaz.* 1852, 466.

Occurs in *Calluna vulgaris*.

*Preparation.* The alcoholic decoction of the comminuted plants is freed from alcohol by distillation; the residue is mixed with water; the filtrate is precipitated with neutral acetate of lead; the washed precipitate is treated with very dilute acetic acid; and the filtered solution is precipitated at the boiling heat with basic acetate of lead, whereby a chrome-yellow precipitate of callutannate of lead is produced. On decomposing this precipitate under water with hydro-sulphuric acid, heating the liquid together with the sulphide of lead to the boiling point, and evaporating the filtrate over a chloride-of-calcium bath in a stream of carbonic acid, callutannic acid remains behind, and may be dried in vacuo over oil of vitriol.

Amber-yellow, inodorous mass.

				Rochleder.	
14 C .....	84 .....	51.53 .....	51.69 .....		
7 H .....	7 .....	4.30 .....	4.58 .....		
9 O .....	72 .....	44.17 .....	43.73 .....		
<hr/>				<hr/>	
$C^{14}H^7O^9$ .....	163 .....	100.00 .....	100.00 .....		

Callutannic acid reduces *nitrate of silver*. — Its aqueous solution heated with *mineral acids*, assumes a reddish yellow colour, and yields yellow flocks of *Calluzanthin*, which, after drying at  $100^{\circ}$ , contains 58.07 p. c. C., 3.77 H., and 38.16 O. ( $C^{14}H^5O^7 = 57.93$  p. c. C., 3.45 H., and 38.62 O.), and, according to Rochleder, is produced from callutannic acid by elimination of 2 at. water. The alkaline solution of this substance readily

absorbs oxygen, and is then precipitated in red-brown flocks by acids. It is soluble in alcohol.

*Stannic Callutannate*. — Warm aqueous callutannic acid added to a solution of stannic hydrochlorate, throws down a beautiful egg-yellow precipitate, soluble in excess of the tin-salt.

at 100°.				Rochleder.	
28 C .....	168	.....	19.33	.....	19.20
16 H .....	16	.....	1.84	.....	2.37
20 O .....	160	.....	18.42	.....	18.40
7 SnO <sup>2</sup> .....	525	.....	60.41	.....	60.03
<hr/>					
2C <sup>14</sup> H <sup>6</sup> O <sup>8</sup> , 7SnO <sup>2</sup> + 4HO ....	869	.....	100.00	.....	100.00

*Callutannate of Lead*. — Preparation, p. 514. Obtained by double decomposition.

a. at 100°.			Rochleder.		b. at 100°.			Rochleder.	
28 C .....	19.18	...	19.01		42 C .....	18.34	...	18.21	
13 H .....	1.48	...	1.68		20 H .....	1.45	...	1.55	
17 O .....	15.54	...	15.37		26 O .....	15.15	...	15.07	
5 PbO ....	63.80	...	63.94		8 PbO ....	65.06	...	65.17	
<hr/>									
100.00			...	100.00	100.00			...	100.00

Rochleder resolves the formula *a* into 2C<sup>14</sup>H<sup>6</sup>O<sup>8</sup>, 5PbO + aq.; *b* into 3C<sup>14</sup>H<sup>6</sup>O<sup>8</sup>, 6PbO + 2aq.

Callutannic acid colours *ferric salts* green. — Aqueous callutannic acid, heated to the boiling point with stannic hydrochlorate and a small quantity of hydrochloric acid, dyes woollen cloth mordanted with alum, sulphur-yellow to orange.

## 5. Catechutannic Acid.

NEES v. ESENBECK. *Repert.* 33, 169; 43, 340.

BERZELIUS. *Lehrbuch*, 3 Aufl. 6, 250.

DELFS. *Jahrb. pr. Pharm.* 12, 164.

STENHOUSE. *Ann. Pharm.* 45, 18.

STRECKER. *Ann. Pharm.* 90, 375.

NEUBAUER. *Ann. Pharm.* 96, 337.

Regarded as a distinct substance by Nees v. Esenbeck and Berzelius, but not known in the pure state. — Occurs in catechu, an extract prepared by boiling the wood of *Acacia Catechu* and *Uncaria Gambir*. On catechu, see also the latest statements of Sacc (*Compt. rend.* 53, 1102), which, however, are in opposition to those of Neubauer.

Catechutannic acid is a product of the decomposition of catechin (xii, 387), not the substance from which the latter is formed: If, as Berzelius recommends, a very concentrated aqueous extract of catechu, prepared in the cold, be mixed with strong sulphuric acid, only a small yellowish precipitate is obtained, which cannot be separated by filtration; and as sulphuric acid likewise precipitates catechin from aqueous extracts prepared with aid of heat, it follows that Berzelius

must have examined a mixture of catechin and catechutannic acid (Neubauer). — When (according to Berzelius and Delffs) finely pulverised Bombay catechu is exhausted with ether, the ethereal extract does not separate into two layers; but, by evaporation in vacuo, or over the water-bath, a brownish mass is obtained resembling gallo-tannic acid. This mass, dissolved in a small quantity of water, evaporated over the water-bath till the ether evaporates, and separated by filtration from green flocks, deposits needles of catechin, which substance is not produced, as Delffs supposes, from the catechutannic acid, but exists ready formed in the extract.

On agitating an ethereal extract of catechu with water, separating the ethereal solution, evaporating it to dryness, dissolving the residue in water, and leaving the catechin to crystallise out, a mother-liquor is left, containing catechutannic acid in the highest degree of purity attainable. If this liquid be precipitated with sulphuric acid, the precipitate washed to a certain extent with sulphuric acid, then pressed and boiled for several hours with dilute sulphuric acid, it dissolves at first, and then deposits brown flocks, till at length the solution retains only a faint red tint. At this stage no sugar can be detected in the solution (Neubauer). Strecker believes that he obtained sugar in this manner.

When aqueous catechin, which does not precipitate solution of gelatin, is boiled for three hours in an open dish, the solution acquires a yellowish brown colour, and becomes turbid. If it be then evaporated to dryness, and the residue taken up with water, the solution then forms a very copious precipitate with gelatin; nevertheless, the catechin is not completely converted into catechutannic acid. (Neubauer; see also xii, 390).

Stenhouse's catechutannic acid is insoluble in water, whether cold or boiling, also in alcohol and ether, and only partially soluble in alkaline liquids. It is precipitated by sulphuric acid, coloured dark brown by boiling dilute sulphuric acid, and precipitates iron-salts olive-brown. It does not yield either pyrocatechin or pyrogallie acid by dry distillation. Delffs' catechutannic acid (contaminated with catechin) deliquesces to a syrup with water; it decomposes quickly when dissolved in alkalis; forms with bichromate of potash a brown precipitate insoluble in ether, with ferric salts a dirty green precipitate, and is completely precipitated by solution of gelatin.

## 6. Cissotannic Acid.

WITTSTEIN. *Repert.* 106, 317; *Pharm. Centr.* 1847, 791. — *Pharm. Viertelj.* 2, 161.

The colouring matter of the leaves of *Vitis hederacea* reddened in autumn.

*Preparation.* The leaves gathered in August are digested for 24 hours with alcohol of 80 per cent., the tincture is separated from the leaves by pressure, filtered, mixed with  $\frac{1}{2}$  water, and the alcohol distilled off. The residue evaporated to an extract, then treated with

cold water, yields a dark-red solution, whilst a crimson powder, Wittstein's altered cissotannic acid, remains behind. On filtering the liquid from this precipitate, and precipitating the filtrate with solution of neutral acetate of lead, there is produced, first a lighter-coloured, then a green, and finally a greenish yellow precipitate, which, when washed with water (but not completely, otherwise it will decompose), forms olive-green cissotannate of lead *a*.—If the liquid, after precipitation with neutral acetate of lead, be mixed with acetic acid till the grass-green precipitate has again acquired a lighter colour, and the supernatant liquid has become reddish, cissotannate of lead *b* remains undissolved, whilst the filtrate, after standing for some time, deposits flocks, and after these are removed, yields, with neutral acetate of lead, the olive-green lead-salt *c*.

Lead-salt.				Lead-salt.			
<i>a</i> .		Wittstein.		<i>b</i> .		Wittstein.	
120 C	25.67	...	25.98	120 C	32.05	...	31.17
75 H	2.67	...	2.40	75 H	3.34	...	3.01
N	0.50	...	0.50	N	0.62	...	0.61
96 O	27.38	...	27.77	96 O	34.18	...	34.56
11 PbO	43.78	...	43.35	6 PbO	29.81	...	30.65
100.00				100.00			

The nitrogen is present as ammonia —  $a = 11\text{PbO}, 6\text{C}^{20}\text{H}^{12}\text{O}^{16} + \text{NH}_3$ ;  $b = 6(\text{PbO}, \text{C}^{20}\text{H}^{12}\text{O}^{16}) + \text{NH}_3$ ;  $c$  contains from 36.4 to 37.5 p. c. lead-oxide. So according to Wittstein.

*Insoluble or unaltered Cissotannic Acid*.—The portion of the alcoholic extract obtained in the preparation of cissotannic acid, which is insoluble in water.

Dense, dark-brown, shining, non-friable mass, having a slightly bitter, astringent taste.

Wittstein.			
mean; at 110°.			
156 C	56.25	.....	55.91
90 H	5.41	.....	5.41
N	0.84	.....	0.84
78 O	37.50	.....	37.84
$\text{C}^{156}\text{H}^{90}\text{NO}^{78}$	100.00	.....	100.00

=  $3(\text{C}^{62}\text{H}^{28}\text{O}^{25}, 3\text{HO}) + \text{NH}_3$ . Contains the nitrogen as ammonia, and 0.31 p. c. ash, which has not been deducted. (Wittstein.)

Chars quietly when heated. — Dissolves with dark brown-yellow colour, in ammonia, and is precipitated therefrom by acids.

*Lead-compounds*.—*a*. By precipitating the dilute alcoholic solution with neutral acetate of lead. Olive-green, pitch-black after drying. — *b*. By precipitating the alcoholic solution with an insufficient quantity of neutral acetate of lead, treating the precipitate with a small quantity of acetic acid, then washing and drying the undissolved matter. *a* contains 36.91, *b* 16.95 p. c. lead-oxide. (Wittstein.)

Altered cissotannic acid forms a dark-green precipitate, with an alcoholic solution of ferric chloride; flocculent precipitates with tartar-emetic and gelatin-solution.

In alcohol of 60 — 80 p. c. it dissolves easily and with blood-red colour.



## 7. Cocatannic Acid.

ALB. NIEMANN. *Dissert. über eine Base in den Cocablättern.* Göttingen, 1860.

Observed by Wackenroder (*N. Br. Arch.* 75, 26), and Gaedeke (*N. Br. Arch.* 82, 141).

When coca-leaves are exhausted with alcohol containing sulphuric acid, for the preparation of cocaine, the tincture digested with hydrate of lime and filtered, the filtrate neutralised with sulphuric acid, and the alcohol distilled off, carbonate of soda throws down the cocaine, which may be removed by shaking up the alcoholic solution with ether, the cocatannic acid then remaining in solution. The remainder of the ether is driven off, the liquid neutralised with dilute sulphuric acid; this acid removed by nitrate of baryta, and the excess of baryta by carbonate of ammonia; and the liquid, after neutralisation, precipitated by neutral acetate of lead. The washed precipitate decomposed under water by hydrosulphuric acid, yields, after the sulphide of lead has been separated by filtration, an aqueous solution of cocatannic acid, having a yellow-red colour, acid reaction, and slightly astringent taste, and leaving when evaporated, a brown-red, amorphous, hygroscopic mass. The cocatannic acid, thus prepared, still retains a small portion of alkali. — Part of the acid remains dissolved in the liquid filtered from the cocatannate of lead, and may be precipitated therefrom by basic acetate of lead, but when separated by hydrosulphuric acid from the lead-salts, it is contaminated with nitric acid.

The acid, heated on platinum-foil, melts, swells up, gives off an empyreumatic odour, and leaves charcoal. — It reduces chromic acid to chromic oxide, precipitates cuprous oxide from *potassio-cupric tartrate*, and metallic gold from *auric chloride*. — It forms a deep red precipitate with aqueous *alkalis*; throws down from *acetate of baryta* a precipitate soluble in acetic acid; from *tartar-emetic*, brown flocks; from *mercurous* and *mercuric nitrate*, dingy yellow precipitates, but does not precipitate *mercuric chloride*. It colours *sesquichloride of iron* brown-green, and precipitates *white of egg*, but not gelatin-solution.

## 8. Euphrasiatannic Acid.

ENZ. *Pharm. Viertelj.* 8, 175.

In *Euphrasia Officinalis*. — The fresh plant is macerated with water for a day, then boiled and pressed, and the filtrate precipitated by neutral acetate of lead. The precipitate, after being washed, is dissolved in acetic acid, and the solution, filtered from sulphate and phosphate of lead, is neutralised with ammonia, which throws down siskin-green euphrasiatannate of lead, which is washed and dried.

Calculation according to Enz.				Enz. at 100°; mean.	
32 C .....	192	.....	28·07	.....	27·92
20 H .....	20	.....	2·92	.....	3·01
17 O .....	136	.....	19·89	.....	19·73
3 PbO .....	336	.....	49·12	.....	49·34
<hr/>					
$C^{32}H^{20}O^{17}, 3PbO$ .....	684	.....	100·00	.....	100·00

## 9. Tannic Acid from Fruits.

BUGNET. *N. Ann. Chim. Phys.* 61, 280.

Known only in combination with iodine. — Occurs in unripe apples, pears, and other fruits, disappearing as the fruit ripens and the proportion of sugar increases. — When the juice of a fruit containing this tannic acid is mixed with starch, and iodine is dropped in, no iodide of starch is formed till all the tannic acid has been converted into the iodine-compound.

*Preparation of the Iodine-compound.* — The expressed and filtered juice of green apples, mixed with tincture of iodine as long as the colour of the iodine is thereby destroyed, yields, after a few seconds, a brown precipitate, which must be washed with large quantities of water.

Yellow amorphous powder, containing 43·0 p. c. C., 3·3 H., 16·17 I., about  $\frac{1}{2}$  p. c. N., and 3 p. c. ash.

The compound is decomposed by boiling with dilute acids, with formation of dextro-glucose. — It is insoluble in water; after it has been boiled for a quarter of an hour, the filtrate does not reduce potassio-cupric tartrate. Insoluble in alcohol.

## 10. Galitannic Acid.



R. SCHWARZ. *Wien. Akad. Ber.* 8, 26; *Ann. Pharm.* 83, 57; *J. pr. Chem.* 58, 126.

*Occurrence.* In the herb of *Galium verum* and *G. aparine*. Known only in combination with water and oxide of lead.

The aqueous decoction of the herb is precipitated with neutral acetate of lead; the precipitate (containing citric, tannic, and inorganic acids) is removed; the filtrate is precipitated with basic acetate of lead; the precipitate decomposed with hydrosulphuric acid; the liquid filtered from the sulphide of lead is precipitated with neutral acetate of lead, to remove the excess of hydrosulphuric acid and any citric acid that may still be present; and the liquid filtered therefrom is treated with basic acetate of lead, whereby a precipitate of a fine yellow colour is obtained, which, when decomposed under water by hydrosulphuric acid, yields aqueous galitannic acid, having a rather bitter,

astringent taste; and acquiring a brown colour when treated with ammonia and the fixed alkalis. It oxidises when the lead-salt is dried at 100°.

*Galitanmate of Lead.*—Galitanmic acid scarcely precipitates neutral acetate of lead, but forms, with the basic acetate, a precipitate of a fine yellow colour, obtained as above described; it exhibits the composition *a*; *b* is obtained in a different way; both are dried at 100°.

	<i>a.</i>	Schwarz.		<i>b.</i>	Schwarz.
70 C.....	17·84	..... 17·65	28 C.....	12·06	..... 12·08
45 H .....	1·91	..... 2·01	21 H .....	1·43	..... 1·53
55 O .....	18·69	..... 18·43	25 O .....	14·44	..... 14·53
13 PbO ....	61·56	..... 61·91	9 PbO ....	72·07	..... 71·86
	100·00	..... 100·00		100·00	..... 100·00

Schwarz resolves the formula *a* into  $3(\text{C}^{14}\text{H}^9\text{O}^{11}, 3\text{PbO}) + 2(\text{C}^{14}\text{H}^9\text{O}^{11}, 2\text{PbO})$ , and *b* into  $2(\text{C}^{14}\text{H}^8\text{O}^{10}, 2\text{PbO}) + 5(\text{PbO}, \text{HO})$ .

Galitanmic acid changes the colour of *ferric hydrochlorate* to a fine green, and forms a dirty brown precipitate with *cupric acetate*.

## 11. Gardeniatannic Acid.

M. v. ORTH. *Wien. Akad. Ber.* 13, 509; *J. pr. Chem.* 64, 10; *Pharm. Centr.* 1854, 897.

*Occurrence.* In Chinese yellow pods or Wongski, the fruit of *Gardenia grandiflora*, proceeding, according to Jessen (*Wien. Akad. Ber.* 14, 249), from a rubiaceous plant.

*Preparation of the first Tannic Acid.*—The bruised pods are exhausted with alcohol of 40°; the extracts are evaporated in a stream of carbonic acid; the oil, which separates on cooling, or on addition of water, is removed by means of a wet filter; and the reddish yellow filtrate is precipitated with solution of neutral acetate of lead, whereby colouring matters and the first tannic acid are precipitated. (The filtrate serves for the preparation of chlororubin.) The precipitate is decomposed under water by hydrosulphuric acid; the solution containing the first tannic acid and a little colouring matter is filtered from the sulphide of lead, which retains a portion of the colouring matter, and again precipitated with neutral acetate of lead; and this precipitate is also decomposed with hydrosulphuric acid, the sulphide of lead then retaining the whole of the colouring matter, and a filtrate being obtained, which, by evaporation in a stream of carbonic acid, and drying in vacuo, yields the first tannic acid.

On boiling the sulphide of lead with alcohol of 40°, the colouring matter is dissolved, and remains as a dark reddish-yellow syrup, when the alcohol is distilled off in a stream of carbonic acid, and the residue dried in vacuo over oil of vitriol. From this syrup ether extracts a substance which, when the ether is evaporated and the residue treated with water, remains as a *reddish yellow resinous colouring matter*, insoluble in water. The residue, boiled with alcohol which removes a small

quantity of yellow colouring matter, then dried at 100°, is the yellow amorphous colouring matter of v. Orth.

*Préparation of the second Tannic Acid.*—The yellow pods, after exhaustion with alcohol, are boiled with water; the extracts are concentrated; a jelly precipitated therefrom by alcohol; this jelly collected on linen; and the filtrate precipitated with neutral acetate of lead. The precipitate is treated with a small quantity of acetic acid; the insoluble portion separated by filtration; and the solution freed from lead by hydrosulphuric acid. The solution filtered from the sulphide of lead, and evaporated over the water-bath, leaves the second tannic acid, which must be dried at 100°.

*Properties.* The first tannic acid is a brown-yellow amorphous mass.

<i>First Tannic acid.</i>		v. Orth.	<i>Second Tannic acid.</i>		v. Orth.
46 C .....	47·26 .....	47·47	46 C .....	52·98 .....	52·67
36 H .....	6·16 .....	6·22	29 H .....	5·56 .....	5·81
34 O .....	46·58 .....	46·31	27 O .....	41·46 .....	41·52
<hr/>			<hr/>		
C <sup>46</sup> H <sup>36</sup> O <sup>34</sup> ....		100·00 .....	100·00	C <sup>46</sup> H <sup>39</sup> O <sup>27</sup> ....	
		100·00		100·00 .....	
				100·00	

After deduction of ash. — The first acid contains, according to v. Orth, 8 at., the second 1 at. water; this he infers from the composition of the lead-salt

*Lead-salt of the first Tannic Acid.* — Prepared by precipitating the warm solution of the acid with basic acetate of lead, then washing and drying at 100°.

					v. Orth.
46 C .....	276 .....	23·3 .....	22·89		
28 H .....	28 .....	2·3 .....	2·34		
26 O .....	208 .....	17·7 .....	17·38		
6 PbO .....	670 .....	56·7 .....	57·39		
<hr/>					
C <sup>46</sup> H <sup>28</sup> O <sup>26</sup> ,6PbO .....		1182 .....	100·0 .....	100·00	

After deduction of the lead-oxide, = C<sup>46</sup>H<sup>28</sup>O<sup>26</sup> (v. Orth). But he appears to have forgotten that the ash may have passed into the lead-salt. (Kr.)

The first tannic acid colours *ferric hydrochlorate* green.

## 12. Hederic Acid and Hederitannic Acid.

POSSELT. *Ann. Pharm.* 69, 62; *Pharm. Centr.* 1849, 257; *Chem. Gaz.* 1849, 92.

In the seeds of ivy (*Hedera Helix*)

*a. Hederic Acid.* — The fresh pulverised seeds are freed from fat by ether; the residue is repeatedly boiled with alcohol; and  $\frac{1}{4}$ th of the alcohol is distilled off from the tinctures, the impure acid then separating from the residue. It is difficult to purify, and was only once obtained pure by gradual deposition from an ether-alcoholic solution.

Soft, white, slender needles and laminae, which give off 5.4 p. c. water at 100° (2 at. ? = 6.25 p. c.). Inodorous. Has a very irritating taste, and slight acid reaction.

				Posselt. mean.
30 C	180	66.66		66.46
26 H	26	9.63		9.45
8 O	64	23.71		24.09
<hr/>				
C <sup>30</sup> H <sup>26</sup> O <sup>8</sup>	270	100.00		100.00

As the atomic weight has not been determined, the formula cannot be calculated with certainty. (Kr.)

Does not melt when *heated*, but gives off a peculiar aromatic odour, and leaves charcoal. Dissolves with splendid purple colour in *oil of vitriol*.

Insoluble in *water*. — The acid expels carbonic acid from carbonates, and forms, with ammonia, potash, baryta, and lime, amorphous gelatinous *salts*, which dissolve in alcohol, but are nearly or quite insoluble in water.

From the alcoholic ammonia-salt, *nitrate of silver* throws down a white precipitate, which dissolves in boiling alcohol, and separates in the crystalline form on cooling.

Hederic acid is soluble in *alcohol*, but insoluble in *ether*.

*b. Hederitannic Acid. — Epheugerbsäure.* — Obtained from ivy-seeds, exhausted by successive treatment with ether and alcohol (for the preparation of hederic acid) by boiling with water. The decoction is mixed with acetic acid and neutral acetate of lead; the precipitate removed; and the filtrate precipitated with ammonia. The fine yellow precipitate, after being but slightly washed (as it is soluble), is decomposed under water with hydrosulphuric acid, and the solution filtered from the sulphide of lead is evaporated; it then leaves the acid, but in an impure state.

Inodorous, amorphous, acid mass, whose aqueous solution becomes coloured during evaporation. It reduces *mercuric nitrate* and *nitrate of silver*. It acquires a fine yellow colour when mixed with *alkalis*, and is precipitated yellow by *ammoniacal lime-salts* and by *baryta-* and *lead-salts*. It colours *ferric salts* dark green, and forms a greenish precipitate with *cupric sulphate*. It is not precipitated by *solution of gelatin*.

### 13. Helianthotannic or Helianthic Acid.

LUDWIG & KROMAYER. *N. Br. Arch.* 99, 1, and 285.

The iron-greening tannic acid of the seeds of the sunflower, *Helianthus annuus*.

The finely pulverised fruits, freed from the husks, are exhausted with boiling alcohol of 90 per cent.; the alcohol is distilled off in a current of hydrogen; the residue is separated by filtration, the filtrate precipitated with neutral acetate of lead; and the precipitate is collected, washed, and decomposed under water by hydrosulphuric

acid. The liquid filtered from the sulphide of lead, and evaporated over the water-bath, leaves the helianthotannic acid as a brownish-yellow amorphous mass, which may be rubbed to a slightly coloured powder. It is redissolved in water and reprecipitated with neutral acetate of lead; the precipitate is decomposed by hydrosulphuric acid; and the filtrate evaporated, a light greenish-yellow amorphous mass then remaining, which yields a yellowish white powder, and no longer becomes moist on exposure to the air.

After drying at  $100^{\circ}$ , it contains 53.27 p. c. C., 5.97 H., and 40.76 O., answering, according to Ludwig & Kromayer, to the formula  $C^{14}H^9O^8$  (calc. 53.50 C., 5.73 H., and 40.77 O.). — Melts when heated, giving off an odour of burnt coffee, together with acid empyreumatic products. — Heated on platinum-foil, it first chars and then burns away. — Nitric acid imparts to aqueous helianthic acid a fine red colour, but on heating the liquid, nitrous vapours are evolved, and the colour disappears. — Cold oil of vitriol colours the aqueous acid red; hot oil of vitriol blackens it. — When boiled with moderately dilute hydrochloric acid in a stream of hydrogen, it is resolved into fermentable sugar and an acid colouring matter. The latter is precipitated by carbonate of lead. When separated from the lead-compound by hydrosulphuric acid, it yields a colourless solution, which leaves, on evaporation a violet residue, changing to bright red when treated with alkalis. — Helianthic acid, when heated with an alkaline cupric solution, does not reduce it. — From an ammoniacal silver-solution, it reduces metallic silver.

The acid dissolves readily in water. It turns yellow when mixed with alkalis, and is precipitated yellow by lime-water. — The latter precipitate turns brown when exposed to the air in contact with excess of lime-water. — The light yellow lead-salt precipitated from the aqueous acid by neutral acetate of lead, and dried at  $100^{\circ}$ , contains 39.5 or 44.24 p. c. lead-oxide; also 32.44 C., 3.28 H., and 20.04 O., answering to the formula  $2(C^{14}H^9O^7, PbO) + PbO, H_2O$ . — The aqueous acid imparts to sesquichloride of iron a splendid dark green colour, changing to violet on addition of ammonia. It does not precipitate ferrocyanide of potassium, or solution of gelatin.

The acid dissolves in alcohol, but not in ether.

## 14. Ipecacuanhic Acid.



E. WILLIGK. — *Wien. Akad. Ber.* 5, 192; *J. pr. Chem.* 51, 404.

The tannic acid of the root of *Cephalis Ipecacuanha*. (*Handbuch* viii, *Phytochem.* 56.) — Pelletier (*Ann. Chim. Phys.* 4, 172; *J. Pharm.* 3, 145; *Schw.* 19, 440); Massonfour (*Bull. Pharm.* 1, 161), and Richard & Barruel (*J. Pharm.* 6, 264), regarded the acid as gallic acid, though it had been already recognised as distinct therefrom by Pfaff.

*Preparation.* The pulverised root is boiled with alcohol of sp. gr. 0.84; the filtered decoction is precipitated with basic acetate

of lead; and the precipitate is washed with alcohol of sp. gr. 0·83 and dissolved in dilute acetic acid. The acetic acid solution mixed with basic acetate of lead, and then with a small quantity of ammonia, yields a precipitate, which is to be washed with alcohol of 98 p. c., suspended in ether, and decomposed by hydrosulphuric acid. The liquid filtered from the sulphide of lead is evaporated in a stream of carbonic acid; the residue is mixed with water, and filtered from the fat which separates; the filtrate is digested with animal charcoal; and the reddish-brown liquid, after being freed from charcoal, is evaporated in a stream of carbonic acid.

*Properties.* Amorphous, reddish brown mass, having a strongly bitter taste. Very hygroscopic.

at 100°.				Willigk. mean.
14 C .....	84 .....	56·37 .....	56·24 .....	56·24
9 H .....	9 .....	6·04 .....	6·23 .....	6·23
7 O .....	56 .....	37·59 .....	37·53 .....	37·53
$C^{14}H^9O^7$ .....				100·00

*Decompositions.* 1. Melts when heated, swelling up, emitting an odour of formic acid, and leaving a difficultly combustible charcoal. — 2. The alkaline solution absorbs oxygen, and acquires a dark black-brown colour. — 3. It reduces mercury- and silver-salts. — 4. It dissolves in oil of vitriol, forming a brown-red solution, which deposits grey flocks on addition of water. — Nitric acid dissolves ipecacuanhic acid, forming a dark reddish-yellow solution, which turns yellow and gives off nitrous gas when heated.

Ipecacuanhic acid is very soluble in water.

*Ipecacuanhate of Lead.* — Dilute aqueous ipecacuanhic acid does not precipitate neutral acetate of lead, but forms with the basic acetate, a brownish white precipitate, which quickly absorbs oxygen, and acquires a darker colour.

The mono-acid lead-salt is precipitated by basic acetate of lead from the tincture prepared with alcohol of sp. gr. 0·85, after it has been freed from all matters precipitable by alcoholic neutral acetate of lead, and mixed with a large quantity of water; and the precipitate is washed with cold water, and dried at 100°. — If the lead-salt thus obtained be dissolved in acetic acid, and the filtrate precipitated with absolute alcohol, or with basic acetate of lead, precipitates are formed, containing  $\frac{2}{3}$ ,  $\frac{6}{7}$  and  $\frac{6}{5}$  at. ipecacuanhic acid to 1 at. lead-oxide.

			a.	b.	c.	d.
14 C .....	84 .....	32·24 .....	32·07 .....	30·17 .....	26·79 .....	35·06
9 H .....	9 .....	3·45 .....	3·43 .....	3·29 .....	2·83 .....	3·84
7 O .....	56 .....	21·50 .....	21·85 .....	19·71 .....	16·82 .....	22·26
PbO .....	112 .....	42·81 .....	42·65 .....	46·83 .....	53·56 .....	38·84
$C^{14}H^9O^7, PbO$ .....	261 .....	100·00 .....	100·00 .....	100·00 .....	100·00 .....	100·00

Other lead-salts contained 41·1 and 45·9 p. c. PbO. Willigk gives the following formulæ: for b,  $6C^{14}H^9O^6, 7PbO + 6aq.$ ; for c,  $2C^{14}H^9O^6, 3PbO + aq.$ ; for d,  $6C^{14}H^9O^6, 5PbO, + 4aq.$

Ipecacuanhic acid colours aqueous ferric salts green, changing to

violet on addition of a small quantity of ammonia, and inky black with a larger quantity. — From *cupric salts*, on addition of ammonia, it throws down a green-black precipitate. It is soluble in *alcohol*, less soluble in *ether*.

## 15. Kinotannic Acid.

BERZELIUS. *Lehrbuch*, 3 Aufl. 6, 258.

GERDING. *N. Br. Arch.* 65, 283; abstr. *Pharm. Centr.* 1851, 305; *Lieb. Kopp. Jahresber.* 1851, 422.

HENNIG. *N. Br. Arch.* 73, 129; abstr. *Pharm. Centr.* 1853, 177. — *N. Br. Arch.* 77, 260; 85, 150.

EISSFELDT. *Ann. Pharm.* 92, 101; *Chem. Centr.* 1855, 110; abstr. *Lieb. Kopp. Jahresber.* 1854, 431.

The tannic acid of African kino (from *Pterocarpus erinaceus*, *Handbuch* viii, *Phytochem.* 72) must be regarded, according to Berzelius and Gerding, as a distinct compound. Hennig regards it as identical with gallotannic acid; he examined the *Kino malabricum* of commerce, which, in his opinion, is the true African kino. Eissfeldt (who obtained crystals of pyrocatechin (xi, 379) from *Kino malabricum* by the action of ether) did not succeed in preparing kinotannic acid either by the process of Berzelius or by that of Gerding; he regards kinotannic acid as perhaps identical with catechutannic acid. — On the reaction of kino, see Nesenbeck (*Repert.* 27, 211) and Hennig; on a jelly from kino, see Redwood (*N. J. Pharm.* 1, 336). — Characters similar to those of kinotannic acid are exhibited by the tannic acid of *Becuibabhi*, the juice of *Myristica Becuhyba*, a Brazilian tree (see Peckolt, *N. Br. Arch.* 107, 163).

1. When the aqueous extract of kino is precipitated by dilute sulphuric acid—the pale red precipitate washed as long as the wash water acquires a sour taste, and then dissolved in boiling water,—the liquid filtered—and the filtrate containing sulphuric and kinotannic acids mixed with baryta-water, till a sample of it no longer precipitates an acidulated solution of chloride of barium,—the filtrate when evaporated in vacuo, leaves kinotannic in the form of a red fissured mass, sparingly soluble in cold, more easily in boiling water, and having an astringent taste. This product, when its aqueous solution is evaporated in contact with the air, becomes, for the most part, insoluble, and when left in contact with the air, separates as a light red precipitate. Its aqueous solution is precipitated by acids, not by carbonate of potash or tartar-emetic. It is soluble in alcohol, insoluble, or nearly so, in ether (Berzelius). Kinotannic acid, precipitated by sulphuric acid, does not yield pyrogallie acid (xi, 398) by dry distillation (Stenhouse, *Ann. Pharm.* 45, 68).

2. Kinotannic acid prepared by the process just described, but freed from sulphuric acid by carbonate of baryta, exhibits, after drying at 100°, a different composition in different preparations (44.77 p. c. C., 4.21 H., and 42.80 C., 3.66 H.), because the sulphuric acid exerts a decomposing action on it. But when the extract of kino is precipitated by a hot solution of isinglass, the flesh-coloured precipitate collected and boiled with alcohol of 95 per cent., and the currant-red solution evaporated in vacuo or by heat, a purer kinotannic acid is obtained in the form of a red, transparent, fissured mass, which, when dried at 100°, contains 48.32 p. c. C., 4.28 H., and 47.40 O. This kinotannic



acid, of Gerding exhibits the following characters:—It chars when heated, but does not yield any pyrogallie acid by dry distillation. When its aqueous solution is left to stand in open vessels, or when oxygen is passed into it at  $20^{\circ}$ — $30^{\circ}$ , it takes up oxygen, loses its rough taste, and deposits kino-red in the form of a light red pulp, the quantity of which increases when the liquid is heated. Its aqueous solution, mixed with *hydrochloric acid*, becomes turbid, and yields after a while a light red precipitate; it is decolorised by *chlorine*, clouded by *nitric acid*, and when heated therewith assumes a yellow colour and yields oxalic acid. It acquires a darker colour on addition of *ammonia* or *potash*, and after a while deposits precipitates. On heating it to the boiling point with *magnesia alba*, the whole of the kinotannic acid is thrown down as a violet-red precipitate, the solution retaining its dark red colour. With *neutral acetate of lead* it forms a reddish grey precipitate, which contains all the tannic acid, is insoluble in *water*, *alcohol*, and *potash-ley*, but dissolves in *nitric acid*. It does not precipitate *ferrous sulphate*. It forms a black-green compound with *ferrie salts*, imparts a faint red colour to *nitrate of silver*, and afterwards reduces it; and forms, with *cuprie sulphate*, a grey precipitate which turns black on standing (Gerding).

3. Kinotannic acid prepared by the second process is a mixture which does not dissolve completely either in cold or in hot water, absorbs oxygen only in presence of potash, and does not at the same time deposit any sediment. On removing the deposit, which forms spontaneously in aqueous extract of kino (and, according to Hennig, contains hyperpectic acid), a red colouring matter (Hennig's *kinoic acid*) remains in solution, together with the tannic acid of the kino, which latter, in the pure state, is identical with gallotannic acid, and exhibits different characters only when impure. If a small quantity of recently precipitated hydrate of lead be added to the filtered aqueous extract, the red precipitate thereby produced contains the kinoic acid; 100 pts. of its organic substance contain 43.65 p. c. C., 3.31 H., and 53.04 O. The filtrate leaves, on evaporation, a yellow residue, the aqueous solution of which precipitates tartar-emetic and ferric chloride, the latter blue-black; and the yellow residue itself yields pyrogallie acid by dry distillation, and is soluble in ether.—When extract of kino is mixed with neutral acetate of lead, precipitates are formed, successively containing less colouring matter and more oxide of lead, till the last contains 32 p. c.  $PbO$ , corresponding to the composition of gallotannate of lead. If a concentrated tincture of kino be mixed with basic acetate of lead by drops, and at intervals of 12—24 hours, till only a few drops run off from the jelly, and if cold water be then poured in, and the whole left to itself till it begins to show colour, the solution contains a large quantity of tannic acid (together with lead and lime, which may be precipitated by oxalic acid). If it be then mixed with hydrate of lead, and evaporated to dryness in a stream of hydrogen, the organic substance of the residue contains 53.16 p. c. C., 3.71 H., and 43.13 O., agreeing with the composition of gallotannic acid (Hennig).

## 16. Kino-red.

GERDING. *N. Br. Arch.* 65, 290.

Aqueous tannic acid kept for several weeks in contact with the air in open vessels, takes up oxygen, and deposits kino-red, which may be freed from undecomposed kinotannic acid by washing with water.

Amorphous, red mass, which turns brown on the surface when dried, and yields a light red powder. Its alcoholic solution is slightly acid. Nearly tasteless. — After drying between 50° and 60°, it contains 37.55 p. c. C., 3.82 H., and 58.63 O.; from another preparation, 34.96 p. c. C., 3.96 H., and 61.98 O., in other cases, about 10 p. c. O. more.

When heated, it yields a small quantity of pyro-acid. It is partially carbonised by oil of vitriol. — Chlorine decolorises it; nitric acid converts it into oxalic acid. — When boiled for some time with strong hydrochloric acid, it dissolves with dark violet colour, and on cooling, or on dilution with water, it deposits kino-brown as a fine dark brown powder, the liquid remaining red. This kino-brown, dried at 100°, contains from 44.77 to 46.17 p. c. C., 4.39 to 4.52 H., has a neutral reaction, and dissolves, with red colour, in alcohol, acetic acid and tartaric acid. It communicates a red or violet colour to stuffs prepared with tin or iron mordants.

## 17. Leditannic Acid.



E. WILLIGK. *Wien. Akad. Ber.* 9, 302; *J. pr. Chem.* 58, 205; *Ann. Pharm.* 84, 363; *Pharm. Centr.* 1852, 790.

ROCHLEDER & SCHWARZ. *Wien. Akad. Ber.* 9, 307; *J. pr. Chem.* 58, 210; *Ann. Pharm.* 84, 366; *Pharm. Centr.* 1852, 790.

*Occurrence.* In the leaves of *Ledum palustre*. — A tannic acid from *Epacris* and another from horse-chesnuts yield a product of decomposition identical with ledixanthin, without being themselves identical with leditannic acid. (Rochleder, *Wien. Akad. Ber.* 44, 493; *Chem. Centr.* 1862, 8.)

*Preparation.* 1. Neutral acetate of lead is added by drops to the aqueous decoction of the leaves, till a sample of the resulting precipitate dissolves completely in acetic acid; the liquid is then filtered, and the filtrate precipitated with basic acetate of lead. The washed precipitate is decomposed by hydrosulphuric acid, and the solution filtered from the sulphide of lead, is evaporated to dryness over the water-bath. — 2. The alcoholic decoction of *Ledum palustre* is precipitated by water, after the alcohol has been distilled off; the liquid is filtered; the filtrate precipitated with neutral acetate of lead; the

precipitate dissolved in dilute acetic acid; the liquid again filtered; and the filtrate precipitated at the boiling heat with basic acetate of lead. If the precipitate, which has a fine yellow colour, be decomposed under water by hydrosulphuric acid, and the solution, filtered at the boiling heat from sulphide of lead, be evaporated in a stream of carbonic acid, leditannic acid remains behind. (Rochleder & Schwarz.)

*Properties.* Reddish, inodorous powder.

				Willigk.	Rochleder & Schwarz.		
				<i>mean at 100°, in vacuo.</i>			
28 C .....	163	...	55.44	...	55.14	...	50.89
15 H .....	15	...	4.95	...	5.11	...	5.46
15 O .....	120	...	39.61	...	39.75	...	43.65
<hr/>							
2C <sup>14</sup> H <sup>6</sup> O <sup>6</sup> + 3 aq.....	303	...	100.00	...	100.00	...	100.00

After deduction of 1.2 p. c. (Willigk), of 2.08 p. c. ash (Rochleder & Schwarz).

Aqueous leditannic acid boiled with dilute *sulphuric* or *hydrochloric acid* (or mixed with cold oil of vitriol), deposits a yellow or red powder, *Ledixanthin*, which, when dried at 100°, contains 60.9 p. c. C., 4.5 IL., and 34.6 O., therefore C<sup>14</sup>H<sup>6</sup>O<sup>6</sup> (calc. 60.87 p. c. C., 4.35 IL., and 34.78 O.), and is produced from leditannic acid by elimination of water. By dry distillation it yields an oil and crystals of pyrocatechin (xi, 379). It dissolves easily in *alkalis*, and when dissolved in alcohol, forms a red-brown precipitate with an alcoholic solution of *neutral acetate of lead*. (Willigk.)

*Leditannate of Lead.* — The aqueous decoction of the leaves is precipitated by neutral acetate of lead; the precipitate is removed; the filtrate is precipitated by basic acetate of lead, and the yellow precipitate *a* is dried at 100°, *b* in vacuo. (Willigk.)

<i>a.</i>		Willigk.		<i>b.</i>		Willigk.	
140 C .....	32.22	....	32.26	98 C .....	28.66	....	28.54
60 H .....	2.30	....	2.49	51 H .....	2.49	....	2.68
60 O .....	18.42	....	18.25	51 O .....	19.89	....	19.84
11 PbO .....	47.06	....	47.00	9 PbO .....	48.96	....	48.94
<hr/>							
10C <sup>14</sup> H <sup>6</sup> O <sup>6</sup> .11PbO.		100.00	....	100.00	7C <sup>14</sup> H <sup>6</sup> O <sup>6</sup> .9(PbO,ILIO).		100.00

Aqueous leditannic acid is coloured dark-green by *ferric hydrochlorate*.

*Stannic Leditannate.* — Aqueous leditannic acid forms a fine yellow precipitate with *stannic hydrochlorate*. (Rochleder & Schwarz.)

	<i>In vacuo.</i>		Rochleder & Schwarz.
28 C .....	168	22.95	23.07
21 H .....	21	2.87	3.05
21 O .....	168	22.95	23.88
5 SnO <sup>2</sup> .....	376	51.23	50.00
<hr/>			
2C <sup>14</sup> H <sup>6</sup> O <sup>6</sup> .5SnO <sup>2</sup> + 2aq. ....	732	100.00	100.00

Leditannic acid dissolves easily in *alcohol* (Willigk).

# 18. Ratanhiatannic Acid.

WITTSTEIN. *Pharm. Viertelj.* 3, 353; 6, 521.

Occurs in common and in *Savanilla Rhatany root*. — Peschier (*N. Tr.* 4, 2, 182; *J. Pharm.* 6, 34; 10, 348) designated as *craneric acid*, a crystallisable acid from rhatany root, to which he attributed the property of decomposing sulphate of baryta. This, according to Wittstein, must have been tyrosin (xiii, 358), while Hlassiwetz *Ann. Pharm.* 119, 202), thinks it probable that phloramine (p. 69) may occur in rhatany root.

The ethereal extract of the pulverised root-bark of *Krameria triandra* (*Handb. viii, Phytochem.* 42), yields, when the ether is distilled off, and the residue dried, a shining dark-red substance, which dissolves in alcohol; with separation of wax. On evaporating the alcoholic extract, the tannic acid remains behind. — When the dry bark powder of *Savanilla Rhatany root* is exhausted with ether—the ether evaporated—the residue exhausted with alcohol of 90 p. c., which leaves the wax undissolved—the filtrate diluted with ten times its bulk of water—a few drops of solution of neutral acetate of lead added—the liquid filtered,—and the filtrate completely precipitated with neutral acetate of lead, ratanhiatannate of lead *b* is obtained.

The acid melts when *heated*, chars, and leaves a very difficultly combustible charcoal, while a watery and oily distillate passes over containing pyrocatechin (xi, 379). (See also Eissfeldt, *Ann. Pharm.* 92, 109; Uloth, *Ann. Pharm.* 111, 217.)—It dissolves, but imperfectly, even in warm water, forming a dirty rose-coloured solution; it dissolves completely on the addition of a few drops of *ammonia*, whereupon *hydrochloric acid* throws down dirty flesh-coloured flakes. When ratanhiatannic acid (separated from the lead-salt by hydrosulphuric acid) is heated for some time over the water-bath with water, to which 5 p. c. *alcohol* has been added, a hard, brown-red resin, Wittstein's *Ratanhia-red*, separates, and on evaporating the remaining liquid, there remains a small yellowish residue, which has a slightly sweet taste, and reduces *potassio-cupric tartrate* when heated therewith. — The aqueous solution is coloured dark-green by *sesquichloride of iron*, then precipitated; it forms a pale flesh-coloured precipitate with *gelatin-solution*, and is coloured paler by *tartar-emetic*, without precipitation.

*Ratanhiatannate of Lead*. — The alcoholic solution of the tannic acid is mixed with a few drops of neutral acetate of lead, and the filtrate is precipitated with excess of neutral acetate of lead. The pale flesh-coloured precipitate is washed and dried at a gentle heat. — Dark red powder, which, after drying at 100°, undergoes no further change.

Calculation according to Wittstein.					Wittstein. mean at 100°.	
					a.	b.
54 C .....	324.0	...	43.83	...	43.73	43.64
24 H .....	24.0	...	3.25	...	3.23	3.21
21 O .....	168.0	...	22.73	...	22.84	22.90
2 PbO .....	223.6	...	30.19	...	30.20	30.25
<hr/> C <sup>54</sup> H <sup>24</sup> O <sup>21</sup> , 2PbO					100.00	100.00

Ratanhiatannic acid dissolves easily in *alcohol* (Wittstein).

## 19. Ratanhia-red.

WITTSTEIN. *Pharm. Viertelj.* 3, 358.

Produced, together with a saccharine substance, by heating ratanhia-tannic acid (p. 529) with sulphuric acid, and purified by precipitating the alcoholic solution with water.

Brown-red, easily friable, tasteless mass.

				Wittstein.
				<i>mean.</i>
12 C .....	72 .....	70.59 .....		70.67
6 H .....	6 .....	5.88 .....		5.74
3 O .....	24 .....	23.53 .....		23.59
<hr/>				
C <sup>12</sup> H <sup>6</sup> O <sup>3</sup> .....	102 .....	100.00 .....		100.00

Insoluble in *water*, but dissolves easily, with ruby-red colour, in *alcohol*.

## 20. Rhamnotannic Acid.

BINSCHWANGER. *Repert.* 104, 58.

Obtained in the preparation of rhamnocathartin (*infra*, vol. xvi), and purified by washing, drying, solution in ether and evaporation. — Greenish yellow, amorphous, easily friable mass. Tastes bitter and astringent. Neutral. — Melts and decomposes when heated, like a non-azotised body. — Nearly insoluble in cold water; somewhat soluble in boiling water, and in aqueous ammonia; forming a golden yellow liquid, which gradually turns brown. With lime-water and potash-ley it forms yellow solutions, which do not change in contact with the air; the former however gradually deposits yellow flocks. The aqueous solution added to neutral or basic acetate of lead, throws down orange-yellow flocks; it colours ferric-salts olive-green and then precipitates them. In tartar-emetic it forms, after some time, a yellow precipitate. Does not precipitate solution of gelatin. — The acid dissolves readily in alcohol and ether.

## 21. Rhodotannic Acid.



R. SCHWARZ. *Wien. Akad. Ber.* 9, 298; *J. pr. Chem.* 58, 202; *Ann. Pharm.* 84, 361; *Pharm. Centr.* 1852, 773; *Chem. Gaz.* 1853, 44.

*Occurrence.* In the leaves of *Rhododendron ferrugineum*.

*Preparation.* The alcoholic decoction of the leaves is freed from alcohol by distillation; the residue is mixed with water; the filtrate is precipitated with neutral acetate of lead; the precipitate is treated with dilute acetic acid; the liquid is filtered from the undissolved portion, and the filtrate, heated to the boiling point, is precipitated with basic acetate of lead. When rhodotannate of lead is precipitated

under water with hydrosulphuric acid, and the solution filtered at the boiling heat from the sulphide of lead is evaporated in a stream of carbonic acid, rhodotannic acid remains, and after being pulverised, may be dried in vacuo over oil of vitriol.

*Properties.* Amber-yellow powder, having a slightly sour astringent taste.

Calculation according to Schwarz.				R. Schwarz.	
56 C	336	55.00		54.91	
27 H	27	4.41		4.61	
31 O	248	40.59		40.48	
$4C^{14}H^6O^7 + 3aq.$				611	100.00
				100.00	100.00

After deduction of 1.5 p. c. ash.

When heated with aqueous *mineral acids*, it yields a reddish-yellow precipitate of *rhodoxanthin*, which, after drying in vacuo, contains 52.40 p. c. C., 4.66 H., and 42.94 O. ( $C^{12}H^{15}O^{17} = 2C^{14}H^6O^8 + HO$ ; calc. 52.06 C., 3.70 H.), and decomposes at  $100^\circ$ .

*Stannic Rhodotannate.* — Aqueous rhodotannic acid forms with stannic hydrochlorate a precipitate of a fine yellow colour.

at $110^\circ$ .				Schwarz.	
140 C	840	22.61		22.39	
87 H	87	2.34		2.96	
97 O	776	20.89		20.42	
27 $SnO^2$	2025	54.16		54.23	
$10C^{14}H^8O^9, 27SnO^2 + 7HO$				3728	100.00
				100.00	100.00

Approximately =  $C^{14}H^8O^{10}, 3SnO^2$ .

*Rhodotannate of Lead.* — Preparation, p. 530. Fine chrome-yellow precipitate, which does not alter at  $100^\circ$ .

at $100^\circ$ .				Schwarz.	
42 C	252	28.21		28.20	
19 H	19	2.13		2.28	
22 O	176	19.70		19.57	
4 $PbO$	447	49.96		49.95	
$3C^{14}H^6O^7, 4PbO + HO$				894	100.00
				100.00	100.00

## 22. Rhustannic Acid.

J. KHITTEL. *Pharm. Viertelj.* 7, 348.

In the leaves of *Rhus Toxicodendron*. — The ethereal extract of the pulverised leaves is shaken up with warm water; the liquid is filtered and set aside for two days; and the new deposit which then forms is removed by a second filtration, and mixed with a small quantity of neutral acetate of lead, to precipitate sulphuric and phosphoric acids. The filtrate is then completely precipitated by neutral acetate of lead, and the precipitate collected, washed, and dried at  $110^\circ$ . — By decomposing the still moist lead-salt under water with hydrosulphuric acid, the aqueous acid is obtained, having a slight bitter taste and acid reaction;

when evaporated it leaves an amorphous, yellowish green varnish. The aqueous acid colours *ferric chloride* dark green, and forms with it a precipitate of the same colour; it colours *tartar-emetic* deep yellow without precipitation, and renders *gelatin-solution* turbid when concentrated.

	Lead-salt.		Khittel.	
18 C .....	108	...	24.00	..... 24.16
14 H.....	14	...	3.12	..... 3.12
13 O .....	104	...	23.12	..... 23.24
2 PbO.....	224	...	49.76	..... 49.48
<hr/>				
$C^{18}H^{14}O^{13}, 2PbO$ .....	450	...	100.00	..... 100.00

### 23. Rubitannic Acid.



C. WILLIGK. *Wien. Akad. Ber.* 8, 18; *J. pr. Chem.* 58, 118; *Ann. Pharm.* 82, 340; *Pharm. Centr.* 1852, 373; *Chem. Gaz.* 1852, 275.

*Occurrence.* In the leaves of *Rubia tinctorum*.

*Preparation.* The aqueous decoction is precipitated with neutral acetate of lead, the precipitate digested with dilute acetic acid; the filtrate precipitated by ammonia, and the resulting precipitate washed with alcohol and decomposed under alcohol of sp. gr. 0.83 with hydrosulphuric acid. The liquid filtered from the sulphide of lead is freed from alcohol by distillation, then mixed with water, and precipitated by basic acetate of lead. The precipitate is decomposed under water by hydrosulphuric acid, and the filtrate evaporated over the water-bath.

Very hygroscopic. — Coloured red-brown by ammonia.

Calculation according to Willigk.				Willigk.
28 C .....	168	..... 42.96	.....	43.09
23 H.....	23	..... 5.88	.....	5.89
25 O .....	200	..... 51.16	.....	51.02
<hr/>				
2C <sup>14</sup> H <sup>8</sup> O <sup>9</sup> + 7aq. ....	391	..... 100.00	.....	100.00

It still retained a small quantity of ash.

*Rubitannate of Lead.* — The decoction prepared from the fresh herb is precipitated with neutral acetate of lead; the precipitate is digested with dilute acetic acid; and for the preparation of the lead-salt *a*, the acetic acid filtrate is precipitated with ammonia; the precipitate is decomposed by hydrosulphuric acid; and the filtrate, after being freed from excess of hydrosulphuric acid, is precipitated with basic acetate of lead. — To prepare the lead-salt *b*, the acetic acid filtrate is precipitated with basic acetate of lead; the precipitate is decomposed under water by hydrosulphuric acid, and the filtrate, after being freed from hydrosulphuric acid, is precipitated with neutral acetate of lead. — The lead-salt *c* is obtained by adding neutral acetate of lead to the decoction of the dried herb, till a sample of the precipitate dissolves completely in acetic acid; removing the precipitate formed up to that stage of the reaction; precipitating the filtrate with neutral acetate of lead; decomposing the precipitate last obtained with hydrosulphuric

acid; heating the filtrate to expel the excess of that reagent; and then precipitating with neutral acetate of lead.

<i>a.</i> at 120°.				<i>b.</i> <i>In vacuo.</i>			
		Schwarz.				Schwarz.	
70 C .....	11·71	....	11·50	56 C .....	20·13	....	19·97
50 H .....	1·39	....	1·42	33 H .....	1·98	....	2·19
55 O .....	12·26	....	12·34	37 O .....	17·73	....	17·79
24 PbO .....	74·64	....	74·74	9 PbO .....	60·16	....	60·05
$C^{70}H^{50}O^{55}, 24PbO$ ....				100·00	....	100·00	....
				$C^{56}H^{33}O^{37}, 9PbO$ ....	100·00	....	100·00
<i>c.</i> at 100°.				Schwarz.			
28 C .....	14·79	.....	14·74				
19 H .....	1·67	.....	1·63				
21 O .....	14·79	.....	14·97				
7 PbO .....	68·75	.....	68·66				
$C^{28}H^{19}O^{21}, 7PbO$ .....				100·00	.....	100·00	

*a* perhaps therefore =  $C^{14}H^{8}O^9, 5PbO + 2aq.$ ; *b* =  $4C^{14}H^8O^9, 9PbO + aq.$ ; *c* =  $2C^{14}H^8O^9, 7PbO + 3aq.$  (Schwarz.)

## 24. Valerotannic Acid.

CZYRNIAŃSKI. *Ann. Pharm.* 71, 21.

When fresh valerian-roots are exhausted with hot absolute alcohol, the tincture precipitated with alcoholic sugar of lead, and the filtrate precipitated with ammonia, lead-salts of two acids are obtained.

*a.* The precipitate formed by neutral acetate of lead, yields, when washed with boiling alcohol, and decomposed under water with hydrosulphuric acid, a tannic acid, which easily decomposes in contact with the air, is coloured red by oil of vitriol, quickly reduces silver-salts, and turns brown when its ammoniacal solution is exposed to the air. This acid does not colour ferric chloride green; it forms, with baryta, a white salt, which turns brown in contact with the air. Its lead-salt, precipitated yellowish-white by neutral acetate of lead, turns green in contact with the air, and contains, on the average, 17·45 p. c. C., 1·86 H., 13·52 O., and 67·17 PbO., agreeing with the lead-salt of an acid,  $C^{14}H^8O^9$ .

*b.* The precipitate obtained with ammoniacal acetate of lead, yields, when decomposed by hydrosulphuric acid, an acid which has a slight sour taste, appears to crystallise when evaporated in a stream of hydrogen, reduces silver-salts like the acid *a*, but does not form an insoluble baryta-salt. The lead-salt, precipitated by basic acetate of lead, contains, on the average, 15·16 p. c. C., 1·68 H., 14·30 O., and 68·86 PbO., corresponding with the lead-salt of an acid,  $C^{12}H^6O^9$ .

## 25. Xanthotannic Acid.

A. FERREIN. *Pharm. Viertelj.* 8, 1.

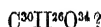
Obtained from elm-leaves reddened in the autumn. The coarsely pulverised dried leaves are exhausted with alcohol; the extract is evaporated and filtered to remove the wax which separates out; the



filtrate is precipitated with water; the liquid again filtered, and then precipitated with neutral acetate of lead. The precipitate is collected (the filtrate yields, with ammonia, another precipitate of the same composition), and decomposed under water with hydrosulphuric acid, whereby an insipid, or if much concentrated, an astringent filtrate is obtained, precipitable by isinglass. — The lead-salt is insoluble in acetic acid.

<i>Lead-salt at 100°.</i>				<i>Ferrein. mean.</i>
28 C .....	168	.....	30.39	..... 29.60
18 H .....	18	.....	3.26	..... 3.21
4 O .....	32	.....	5.79	..... 6.06
3 PbO .....	336	.....	60.56	..... 61.13
<hr/>				
$C^{30}H^{18}O^4, 3PbO$ .....	554	.....	100.00	..... 100.00

## 26. Xylochloric Acid.



L. BLEY, JUN. *N. Br. Arch.* 94, 129.

A green colouring matter, which sometimes forms on decayed pieces of wood, and makes the whole mass appear green. Pieces of wood of this kind do not undergo any change in water, alcohol, or ether, but impart the green colour to alkaline liquids.

*From Beechwood.*—When the colouring matter is extracted from the green wood by twice treating it with aqueous ammonia of the strength of 5 per cent., and the olive-green filtrate is mixed with hydrochloric acid, dark green flocks are precipitated, which, after being washed with water, dry up to a dark green friable mass. This substance is decomposed by heat, giving off acid vapours without melting; it is insoluble in water, alcohol, and ether, is not perceptibly altered by hydrochloric acid, but is carbonised by oil of vitriol. It still contains ash, nitrogen, and water.

The ammoniacal solution of this (impure) xylochloric acid, has a deep olive-green colour, is neutral after the excess of ammonia has been expelled, and yields, by spontaneous evaporation, a residue completely soluble in water. It forms a dingy green precipitate with ferric chloride, olive-green with cupric sulphate and mercurous nitrate, and precipitates nitrate of silver, after some time only, with partial reduction of the silver. When it is precipitated by neutral acetate of lead, the supernatant solution appears colourless, and the dingy green flocks from different preparations exhibit, after drying at 110°, whereby they lose 10 p. c. of their weight, the composition *a* and *b*.

<i>Calculation according to Bley.</i>		<i>Bley. a.</i>	<i>Calculation according to Bley.</i>		<i>Bley. b.</i>
30 C .....	25.67	.... 25.91	90 C .....	25.49	.... 25.38
26 H .....	3.71	.... 3.85	30 H .....	1.42	.... 1.48
34 O .....	38.79	.... 38.57	54 O .....	20.40	.... 19.63
2 PbO .....	31.83	.... 31.67	10 PbO .....	52.69	.... 53.51
<hr/>					
$C^{30}H^{26}O^{34}, 2PbO$ ....	100.00	.... 100.00	$3C^{30}H^{10}H^{18}, 10PbO$ ....	100.00	.... 100.00

# ADDENDA.

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Page 3.

*Pyrrol-red.* — O. Hesse has observed this substance among the products of the putrefaction of yeast (*J. pr. Chem.* 70, 44). On distilling the putrefied yeast at a moderate heat, a large number of fatty acids, volatile bases, &c., are given off; and on subjecting the residue to dry distillation, amylamine and ammonia are evolved, together with a substance, which, when its hot solution is mixed with hydrochloric acid, is immediately converted into a thick, red, amorphous mass of pyrrol-red; hence it appears probable that pyrrol is formed in the decomposition of the carcasses of infusoria.

The pyrrol-red obtained as above, after being well washed and dried in vacuo, formed a black shining mass, which yielded a coffee-coloured powder; it was sparingly soluble in water, ether, acids, and ammonia, easily in alcohol. It gave, by analysis, 66.6 p. c. carbon, 7.1 hydrogen, and 8.8 nitrogen; also a small quantity of sulphur, probably an impurity arising from the decomposition of some of the other products of the putrefaction of the yeast.

Page 57.

*Appendix to Physodin.*

## Ceratophyllin.

O. HESSE. *Ann. Pharm.* 119, 365.

Occurs, together with physodin, in *Parmelia ceratophylla*, var. *physodes* (also called *Parmelia physodes*).

*Preparation.* About 3 lbs. of the lichen, after being washed with water, is stirred up with clear lime-water; the alkaline solution is neutralised with hydrochloric acid; and the resulting yellowish grey flocculent precipitate is washed several times with cold water to remove the excess of acid, then collected, dried in the air, and freed from uncrystallisable matter by digestion with boiling alcohol of 75 p. c. There then remains a dark green, soft, elastic mass, probably containing physodin and usnic acid, to remove which, the mass is boiled with strong soda-ley. A dark brown liquid is thus obtained, which, on cooling, deposits ceratophyllin unmixed with either of the substances

just mentioned. It may be separated from the mother-liquor by filtration, and purified by recrystallisation from boiling alcohol with the aid of animal charcoal. When the lichen, without previous washing, is stirred up with thin milk of lime, the yellowish filtrate does not yield any precipitate with hydrochloric acid. The precipitate formed as above described is particularly abundant when the lichen has been obtained from birch-stems, and the maceration has not been continued for more than 15 hours.

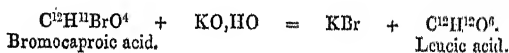
*Properties.* Thin, white prisms, which when placed upon the tongue produce, at first, a slightly irritating taste, soon becoming rather strongly perceptible in the throat; subsequently a persistent burning sensation is experienced on the tongue. Melts at  $147^{\circ}$  to a colourless liquid, and solidifies in the crystalline form between  $136^{\circ}$  and  $138^{\circ}$ . It begins to sublime even at the melting point, and at a somewhat higher temperature sublimes very easily and without alteration in thin, colourless laminae.

Ceratophyllin appears to be a higher homologue of orsellate of ethyl,  $C^{20}H^{12}O^8$  (xii, 373); its melting point is about  $15^{\circ}$  degrees higher than that of the latter.

Ceratophyllin is much more soluble in hot water than in cold; it dissolves readily in alcohol, ether, potash-ley, aqueous ammonia, and lime-water. The alcoholic solution, which has a neutral reaction, is coloured purple-violet by a small quantity of ferric chloride, blood-red by solution of chloride of lime, the latter colour being destroyed by excess of the reagent; no precipitate with alcoholic sugar of lead or nitrate of silver. From the ammoniacal solution, hydrochloric acid throws down the ceratophyllin in thin prisms. Ceratophyllin dissolves in dilute nitric acid, the solution acquiring only a slight yellow tint when heated. Strong sulphuric acid dissolves it without alteration at ordinary temperatures, but chars it when heated.

#### Page 58.

*Leucic Acid.*—This acid is produced by the action of potash or of silver-oxide on bromo-caproic acid (Cahours, *Ann. Pharm. Suppl.* 2, 78):



#### Page 73.

*Starch-granules in the Atmosphere.*—Pasteur, by drawing air for some time through a tube containing a plug of gun-cotton, to arrest the particles of dust carried along by the current, then dissolving up the cotton with ether-alcohol, leaving the dust to settle, decanting the liquid, washing the dust several times with ether-alcohol, and then testing it under the microscope with iodine-water,—has shown that starch-granules constantly exist in the atmosphere. — Starch-granules are also found in the dust which settles on floors, furniture, &c. (*N. Ann. Chim. Phys.* 64, 29).

## Page 83.

*Starch*, heated with bromine and water, yields a solution which no longer contains free bromine, but does not yield any crystallised acid like isobiglycolethyleneic acid (p. 233), or any other crystallisable compound (Barth & Hlasiwetz, *Ann. Pharm.* 122, 111).

## Page 135.

*Cellulose* (cotton), treated in like manner with bromine and water, is partially dissolved, but yields only traces of an acid syrup (Barth & Hlasiwetz, *loc. cit.*).

## Page 175.

*Spontaneous Decomposition of Pyroxylin under the influence of diffused light.*—(Bonet, *Compt. rend.* 53, 405; *Zeitschr. Ch. Pharm.* 5, 96.)—Two samples of pyroxylin, (*a*) prepared with a mixture of sulphuric acid and nitrate of potash, (*b*) with nitro-sulphuric acid, and both kept in stoppered bottles exposed to diffused daylight, underwent spontaneous decomposition in the course of four years; *a* decomposing more quickly than *b*, and with much greater energy. In both cases the decomposition was accompanied by the evolution of red vapours, which showed themselves before the decomposition was complete.

The solid residue of *a* was porous, having the appearance of a substance which had been more or less fluid; that of *b* was compact, hard, and elastic, had more or less of a gummy aspect, and a yellowish white or straw-yellow colour; the colour of the residue *a* was darker, like that of sugar somewhat considerably caramelised.

In both cases the sides of the bottles were covered with crystals of oxalic acid (*comp. Hofmann*, p. 175); the residue of *b* was also penetrated by these crystals in several places.

The atmosphere above the residue *b* was strongly acid, and contained carbonic and formic acids, together with a vapour which had a great attraction for water. Some indications of the presence of cyanogen were likewise obtained; but they were not decisive. The gas did not give any indications of the presence of either of the oxygen-compounds of nitrogen, not even of nitric oxide.

The solid residue freed from oxalic acid by alcohol, left a white substance, perfectly soluble in water, like gum.

According to Chevreul (*Compt. rend.* 53, 407), pyroxylin may be kept in the dark for ten years without decomposing.

## Page 254.

*Conversion of Cane-sugar into Glucose by the action of Acids.*—Löwenthal & Lenssen (*J. pr. Chem.* 85, 321) have examined the manner in which this reaction is affected by variations in the proportions of acid, sugar, and water present, as well as by the duration of the process and the temperature at which it takes place. All the experiments were made at the atmospheric temperature, excepting those

in which the effect of change of temperature was the special object studied.

1. The intensity of the action of sulphuric acid upon sugar diminishes as the quantity of acid increases up to a certain point, after which it increases in proportion to the quantity of acid used.— 2. The action is proportional to the quantity of *sugar* present. The same quantity of acid, treated with increasing quantities of aqueous cane-sugar, was found to yield quantities of glucose, varying from 3.49 to 3.56 per cent. of the sugar employed.— 3. The intensity of the action diminishes to a certain point as the solution is more dilute; but beyond that point the intensity of the action increases with the degree of dilution.— 4. In the early stages of the reaction its intensity continually increases, but as soon as 2 at. glucose have been formed for every 5 at. acid, it progressively diminishes.

A solution of cane-sugar left to itself for about a fortnight, is found to contain glucose; no alteration is however perceptible in it at the end of 24 hours, even if it has been kept at the boiling heat, but if it be heated under pressure with a small quantity of acid, a very energetic action takes place, increasing with the temperature.

All *monobasic mineral acids* modify sugar in the same degree. The neutral salts of these acids, on the contrary, have no action upon it; nevertheless, their presence accelerates the action of acids on saccharine solutions: thus the transformation of cane-sugar into glucose by hydrochloric acid takes place much more quickly on the addition of chloride of calcium. The neutral salt however acts only when at least 2 molecules of acid are present to 5 molecules of the salt; moreover its effect is limited to the earlier stages of the action; after the lapse of a few hours, the action goes on as if there were no neutral salt present.— Nitric, hydriodic and chloric acids, act in presence of their neutral salts in the same manner as hydrochloric acid with chloride of calcium.— Löwenthal & Lenssen attribute the effect of neutral salts to their power of combining with a portion of the water, and thus increasing the strength of the acid.

Page 290.

*Colloidal\* condition of Sucrates.*— (Graham, *Chem. Soc. J.* 15, 255).

\* The term *colloidal* is applied by Graham to a class of bodies—of which gelatin may be regarded as the type—which possess but little diffusibility,—form gelatinous hydrates,—are remarkably inactive in their chemical relations,—incapable of crystallising,—and though largely soluble in water, are yet retained in it by a very feeble force.— Such are aqueous silicic acid, aqueous alumina, starch, dextrin, the gums, caramel, tannin, albumin, gelatin, vegetable and animal extractive matters.— Those substances, on the contrary, which are capable of crystallising and exhibit a high degree of diffusibility are called *crystalloids*. Liquid colloids appear to have always a pectous or curdled modification, and often pass into that condition under the slightest influences. Many solid colloidal substances, such as the jelly of starch, that of animal mucus, of vegetable gelose, &c., are easily permeable to crystalloidal substances, but offer great resistance to the passage of colloids, like themselves. Hence a septum of such substance affords an excellent means of separating crystalloidal from colloidal substance, in solution. A very convenient apparatus for the purpose consists of a sheet of parchment-paper stretched over a hoop like a drum, which is then caused to float upon a large quantity of pure water, the mixed colloid and crystalloid solution being poured upon its upper surface. Such an apparatus is called a “dialyser,” and the separation of crystalloids from colloids in this manner is called “dialysis.”

*Sucrate of Lime.* — The solution of lime in sugar forms a solid coagulum when heated, and at a high temperature is probably entirely colloidal. The solution obtained on cooling passes through a septum of parchment-paper, but requires a much longer time than a true crystalloid like chloride of calcium.

*Sucrate of Uranyl.* — A colloidal compound is obtained by adding potash to a mixture of uranic nitrate or chloride with sugar, avoiding heat. The solution is of a deep orange colour, and on the dialyser soon loses the whole of its acid and alkali. The fluid sucrate has considerable stability, but is readily *pectised* (coagulated) by salts, with separation of a basic sucrate which is soluble, to a considerable extent, in pure water.

*Ferric Sucrate.* — Ferric chloride mixed with sugar is not precipitated by potash, provided the temperature is not allowed to rise. The ferric oxide combined with the sugar is colloidal and remains without loss on the dialyser. At a certain stage, however, the sugar appears to leave the ferric oxide; a gelatinous ferric subsucrate pectises. The basic sucrate thrown down from the soluble sucrate by the addition of sulphate of potash, consisted of about 22 pts. sugar, to 78 pts. ferric oxide.

*Cupric Sucrate.* — The deep blue liquid obtained by adding potash to a mixed solution of cupric chloride and sugar, appears to contain a colloidal substance. It loses by dialysis the whole of its potassium and chlorine, a colourless liquid passing through the dialyser, and a green liquid remaining, consisting of a compound of sugar with cupric oxide. This solution, when mixed with salts or acids (even acetic acid) deposits a bluish-green pectous precipitate (containing about 1 pt. sugar to 2 pts. cupric oxide); when heated strongly, it also yields a bluish green precipitate, and does not allow the protoxide of copper to be easily reduced to dioxide. When evaporated, it leaves transparent emerald-green films, which are not altered by alcohol either cold or boiling, but are resolved by water into sugar and the pectous bluish-green compound above-mentioned.

The blue solution of cupric tartrate in caustic potash contains a colloidal compound which has not yet been fully examined.

### Page 291.

*Caramelane.* (Gélis, *N. Ann. Chim. Phys.* 65, 497.) — This substance may be obtained quite colourless, by operating on starch-sugar [? by heating it for some time to 190°, and operating as described at page 291] and decolorising the product with *crude* animal charcoal. This colourless caramelane, as well as the coloured product described at page 291, is not capable of reproducing sugar.

If caramel be prepared without attention to the precautions indicated by Gélis [heating sugar for some time to a temperature not below 190°], if, for example, the heat is too low, or not continued long enough, the portion of the caramel which is soluble in alcohol, contains a large quantity of glucosan as well as caramelane. Glucosan is likewise colourless, and is distinguished from caramelane by its power of reproducing the sugar from which it was derived, when subjected to certain

influences, especially to the action of water or dilute acids. This property, already noticed by Gélis (*N. Ann. Chim. Phys.* 57, 234), explains a fact recently observed by Pohl, (see p. 249) namely, that certain caramels regain their saccharine taste by keeping.

### Page 293.

*Caramel* (Graham, *Chem. Soc. J.* 15, 258). — When crude caramel, obtained by heating cane-sugar to  $210^{\circ}$  —  $220^{\circ}$ , is placed on the dialyser, certain colouring matters of intermediate composition, the caramelane and caramelene of Gélis pass through, and caramelin, the most highly carbonised compound of the three, remains behind. This purified caramel (which may also be obtained from crude caramel, by repeatedly precipitating the aqueous solution with alcohol till the precipitate is no longer plastic, but pulverulent,) possesses five times the colouring power of the original caramel. A solution containing 10 per cent. of it is gummy, and changes, on standing, to a jelly perfectly soluble both in hot and in cold water; the solution dries up in vacuo to a black shining mass, which, so long as it retains a certain amount of water, is still tough and elastic. If this purified caramel be carefully dried at a comparatively low temperature, it remains soluble in water after being heated to  $120^{\circ}$ , but if the solution be at once evaporated to dryness at  $100^{\circ}$ , the caramel becomes insoluble both in cold and in hot water. Purified caramel gave, by analysis, 54.59 p. c. carbon, answering nearly to the formula  $C^{24}H^{13}O^{13}$ , which requires 55.17 p. c.; Gélis (*N. Ann. Chim. Phys.* 52, 377, obtained in two analyses of his caramelin 55.06 and 55.11 p. c. carbon).

A solution of pure caramel (caramelin) is tasteless, and has a neutral reaction. The caramel is precipitated from it by the smallest quantity of mineral acids, alkaline sulphides, chloride of sodium, and most other salts, and by alcohol, as a brownish black, pulverulent substance, insoluble in water, whether cold or hot. In the crude product of the roasting of sugar, the caramel is protected from the action of these bodies by the intermediate brown substances present. The caramel, thus rendered insoluble, swells up to a jelly in dilute potash-ley, and dissolves when the liquid is warmed. On dialysing this solution, the proportion of potash in it is quickly reduced to about 9 per cent., and if acetic acid be then added, the whole of the potash passes through the dialyser, and pure caramel remains behind.

### Page 357.

#### *Mannite in the Olive.*

DE LUCA. *Compt. rend.* 55, 506.

Mannite exists in all parts of the olive, especially in the leaves, flowers, and fruits of the olive, in quantities varying with the season.

The leaves when macerated for some days in strong alcohol, give up water, which passes into the alcoholic solvent, and at the same time mannite separates out upon their surface in stellate groups of silky needles. When the leaves are treated with boiling alcohol, the liquid,

on cooling, deposits mannite mixed with other substances soluble in alcohol.

The leaves in the earlier stages of their growth contain but a small quantity of mannite; it increases as they develop, but diminishes during the flowering time, and while the leaves are beginning to assume their green tint; and disappears entirely when they turn yellow and fall off.

The following table shows the quantities of mannite obtained from the leaves of different olive trees, growing in the neighbourhood of Pisa.

	Time of Gathering.	Weight of Leaves.		Mannite obtained.	
		Moist.	Dry.	Total.	Per cent.
		grms.	grms.	grms.	grms.
1.	5 November, 1861.....	265·0	139·1	0·597	0·43
2.	12       "       " .....	120·0	100·3	0·128	0·12
3.	19       "       " .....	430·0	209·8	0·972	0·61
4.	28       "       " .....	104·0	95·0	0·253	0·26
5.	7 December, 1861.....	222·0	116·3	1·468	1·25
6.	14       "       " .....	225·0	139·5	1·005	0·72
7.	24       "       " .....	140·0	106·9	0·394	0·37
8.	6 January, 1862.....	263·0	164·3	0·583	0·36
9.	16       "       " .....	198·0	126·3	1·065	0·84
10.	26       "       " .....	324·0	177·2	1·425	0·71
11.	4 February, 1862.....	350·0	212·1	0·872	0·41
11 bis.	4       "       " .....	418·0	212·7	1·506	0·70
12.	14       "       " .....	324·0	229·3	1·286	0·56
13.	21       "       " .....	381·0	157·9	0·375	0·23
14.	1 March, 1862.....	139·0	124·7	0·837	0·67
15.	12       "       " .....	97·0	49·5	0·333	0·67
16.	23       "       " .....	171·0	130·8	0·545	0·42
17.	4 April, 1862.....	155·0	127·9	0·060	0·05
18.	14       "       " .....	167·0	163·7	0·424	0·26
19.	25       "       " .....	97·0	90·8	0·035	0·04

The next table gives the quantities of mannite obtained from leaves, gathered on the 26th of February, 1862, from 13 different olive-trees growing in the Botanic Garden at Naples,



	Time of Gathering.	Weight of Leaves.		Mannite obtained.	
		Moist.	Dry.	Total.	Per cent.
		grms.	grms.	grms.	grms.
1.	26 February, 1862 .....	102·0	52·0	0·285	0·55
2.	" " .....	140·0	67·2	0·901	1·32
3.	" " .....	126·0	64·0	0·525	0·82
4.	" " .....	165·0	87·9	1·360	1·54
5.	" " .....	141·0	70·9	0·874	1·23
6.	" " .....	122·0	66·6	0·440	0·66
7.	" " .....	78·0	38·1	0·232	0·61
8.	" " .....	95·0	50·1	0·514	1·03
9.	" " .....	103·0	56·2	0·710	1·26
10.	" " .....	120·0	65·7	0·724	1·10
11.	" " .....	125·0	65·0	0·680	1·04
12.	" " .....	105·0	56·6	0·489	0·86
13.	" " .....	131·0	63·9	0·853	1·33

The percentage of mannite is calculated on the leaves dried between 110° and 120°.

A comparison of the two tables shows that the leaves of olives grown at Naples contain a larger quantity, than those grown at Pisa, and gathered at the same time of year.

The *flowers* of the olive, in the month of June, contain a considerable quantity of mannite, which may be extracted by alcohol, but after fecundation it disappears altogether from the flowers, so that those which fall on the ground contain none.

The *fruit* of the olive, even when scarcely formed, contains a considerable quantity of mannite, so that when young olives, which can scarcely be separated from the flower, are immersed for some time in alcohol, the liquid spontaneously deposits mannite, and the mother-liquor yields an additional quantity when evaporated to a third of its bulk. — The olives are found to contain mannite so long as they remain green; but the quantity continually diminishes as they approach maturity, and disappears altogether when they are quite ripe and no longer green, and contain their maximum quantity of oil.

Chlorophyll, or an analogous green substance, which constantly accompanies mannite in the leaves and fruit of the olive, likewise disappears simultaneously with it, so that the yellow leaves and the ripe olives contain neither mannite nor chlorophyll. The increase of the proportion of these two substances, during the period of development of the fixed oil, and their disappearance when the olives contain their maximum of oil, seems to show that they contribute in some way to the formation of the fatty matter.

When the alcoholic solution of mannite, obtained either from the leaves or from the fruit of the olive, has deposited the whole of the crystallisable mannite, the mother-liquor, if left for some weeks to evaporate in the air, is converted into a viscous substance, which gradually yields a fresh crop of crystals of mannite separable by boiling alcohol. This seems to show, that the mannite in the leaves and fruit is accompanied

by mannitan, which, on exposure to the air, takes up the elements of water, and is converted into mannite.

Pages 384, 389.

*Identity of Melampyrite and Dulcite.*

L. GILMER. *Ann. Pharm.* 123, 372.

ERLENMEYER & WANKLYN. *Chem. Soc. J.* 15, 455.

The identity of these two bodies is shown by comparison of their crystalline forms, composition, and reactions.

Melampyrite (from *Melampyrum nemorosum*), crystallises from a moderately warm aqueous solution in transparent, colourless, shining prisms, of the oblique prismatic (monoclinic) system, with octahedral summits, the edges of which are truncated by the faces of an orthodigonal dome, or the combination by  $\infty P. + P. - P. + P\infty. - P\infty.$  Inclinations of the faces,  $\infty P : \infty P = 112^\circ$ ;  $+ P : - P = 115^\circ 45'$ ;  $\infty P : + P = 134^\circ 45'$  (Gilmer).

The crystals of dulcite are described by Laurent as monoclinic prisms, having their obtuse edges symmetrically truncated, together with the octahedral, and the basal end-faces.  $\infty P : \infty P\infty : + P. - P. o P.$  Inclination of  $\infty P : \infty P = 112^\circ$ ;  $+ P : - P = 115^\circ 26'$ ;  $\infty P. + P = 134^\circ 42'$  (see page 385). The crystals of dulcite and melampyrite are therefore identical, so far as regards their primary forms and chief modifications; in both bodies also they are generally aggregated in crusts. Both are slightly sweet, optically inactive, and not capable of fermenting with yeast.

The melting point of melampyrin, as determined by Gilmer, is  $180^\circ$  (uncorrected); according to Eichler (p. 390) it is  $186^\circ$ ; that of dulcite is  $190^\circ$  (Laurent);  $182^\circ$  (Jacquelin). Both bodies crystallise from fusion.

The composition of melampyrite, agrees with the formula of dulcite,  $C^{12}H^{14}O^{12}$ , a result corroborated by the analysis of the baryta-compound.

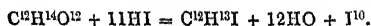
<i>Melampyrite, at 140°.</i>				Gilmer.	Erlenmeyer & Wanklyn.			
12 C.....	72	.....	39.56	.....	39.46	....	39.7	.... 39.33
14 H.....	14	.....	7.69	.....	7.87	....	7.9	.... 7.90
12 O.....	96	.....	52.75	.....	52.67	....	52.4	.... 52.77
$C^{12}H^{14}O^{12}$ .... 182				..... 100.00	..... 100.00	.... 100.0	.... 100.0	.... 100.00

<i>Baryta-compound, at 140°.</i>				Gilmer.			
12 C.....	72	.....	22.7	.....	22.4	.....	22.4
12 H.....	12	.....	3.8	.....	4.1	.....	4.1
10 O.....	80	.....	25.2	.....	23.6	.....	23.6
2 BaO.....	153	.....	48.3	.....	49.9	.....	49.9
$C^{12}H^{12}Ba_2O^{12}$ ..... 317				..... 100.0	..... 100.0	..... 100.0	..... 100.0

<i>Baryta-compound dried over oil of vitriol.</i>				Gilmer.	
12 C .....	72	.....	18.0		
12 H.....	12	.....	3.0		
10 O .....	80	.....	20.3		
2 BaO.....	153	.....	38.4	.....	38.6
9 HO .....	81	.....	20.3	.....	20.0
<hr/>				<hr/>	
$C^{12}H^{12}Ba^2O^{12} + 9aq.$ .....	298	.....	100.0		

The baryta-compound of dulcite, air-dried, contains  $C^{12}H^{12}Ba^2O^{12} + 14aq.$  (not  $C^{12}H^{14}O^{12}.2BaO + 14aq.$ , as stated at page 387). (*Lieb. Kopp. Jahresber.* 1850, p. 536.)

Melampyrite heated to  $275^{\circ}$  begins to give off water, the mass at the same time assuming a brownish tint; [dulcite appears to decompose at a somewhat lower temperature (p. 385)]. — Melampyrite heated with *nitric acid* yields a considerable quantity of mucic acid; the liquid filtered therefrom, and neutralised with carbonate of lime, yields a precipitate, consisting chiefly of oxalate of lime, and the solution, filtered from this precipitate, contains a substance which reduces an alkaline cupric solution. Dulcite yields the same products together with racemic acid (p. 386); the formation of the latter was not observed in the case of melampyrite, probably because the quantity operated on was not sufficient. (Gilmer.) — Melampyrite heated in a stream of carbonic acid with *hybridic acid* yields iodide of caproyl (hexyl), together with water and free iodine (Erlenmeyer & Wauklyn).



One pt. dulcite dissolves in 31.25 pts. water at  $15^{\circ}$ ; 1 pt. melampyrite dissolves in 29.41 pts. water at  $16^{\circ}$  (Gilmer); in 34.01 pts. at  $16.5^{\circ}$  (E. & W.). Both bodies are but slightly soluble in *alcohol*. (Gilmer.)

Melampyrite and dulcite form, with *sulphuric acid*, conjugated acids, the baryta-salts of which exhibit similar properties (pp. 386, 392).

END OF VOL. XV.

REPORT  
OF  
THE FOURTEENTH ANNIVERSARY MEETING  
OF THE  
CAVENDISH SOCIETY.

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THE Anniversary Meeting of the Cavendish Society for the year 1861, was held at the rooms of the Chemical Society, in Burlington House, on Friday the 1st of March, at three o'clock in the afternoon.

The Chair was taken by THOMAS GRAHAM, Esq., F.R.S., President, who called upon the Secretary to read

THE REPORT OF THE COUNCIL.

"In submitting the Annual Statement of their Proceedings to the Members of the Cavendish Society, the Council trust it will be found that satisfactory progress has been made in carrying out the object to which their efforts have recently been chiefly directed—of completing at as early a period as possible the translation of GMELIN's 'Handbook of Chemistry.' The generally expressed opinion of Members, and the decision of previous Councils, have been favourable to the adoption of this course; and the undiminished support afforded by Subscribers during the past year has enabled the Council to proceed in it with as much expedition as the rate of production of the German edition of the work would admit. The fourteenth

volume, comprising organic compounds with twenty and twenty-two atoms of carbon, has just been completed, and is now being distributed to Subscribers for the year 1860. The remaining portion of the work will occupy two more volumes, and there is every reason to believe that these will be produced with the regularity which has marked the progress of the publication of the work for several years past. The Members may, therefore, anticipate the satisfaction of seeing this—their great—work brought to a conclusion in about two years from the present time. Arrangements have also been made for the preparation of a complete index to the work, which Mr. WATTS has undertaken, and which, if the Members continue to give the requisite support to the Council, may constitute a second volume for the year in which the work is finished.

“During the progress of the translation of the organic part of the work, it has been found necessary in some of the later volumes to introduce much new matter belonging, according to the arrangement adopted, to preceding volumes, and resulting from investigations made since their publication. In volumes nine, ten, twelve, and thirteen there are 377 pages devoted to such additional matter, forming appendices to those which preceded, and there will probably be a still greater quantity of matter to be added to the two remaining volumes to bring even the organic part of the work up to the then existing state of chemical knowledge. So rapid, indeed, is the progress of discovery in this prolific department of chemistry, that when the last volume of GAYLUS’s work has been prepared, it is estimated, if the three departments of inorganic and organic chemistry and chemical physics be included, that there will be a sufficient amount of new matter to make a volume annually of the size of those hitherto issued. It will be a question for the consideration of the Members and of future Councils whether the annual publication of all new matter, condensed and arranged in the way in which this was originally so ably done by LEOPOLD GAYLUS, and has since been continued by Mr. WATTS, would not constitute a work to which the Cavendish Society might apply their means with advantage. The expense of preparing such a work would be rather greater than that of merely translating, and it could only be undertaken in the event of an increased number of Subscribers

manifesting a disposition to support the Council in carrying out this object if it should be thought desirable.

"It will be observed on reference to the financial statements for this and previous years that the income of the Society has to some extent been derived from the sale of books which were issued several years ago, and of which more copies were printed than were required to supply the Members. The arrangements under which this distribution of the surplus copies of some of the Society's works has been effected, has fully answered the purpose contemplated; a large number of valuable scientific works have been brought within the reach of chemists who could not otherwise have obtained them, and increased means have been afforded the Society for extending its operations by the production of new books. With reference to the early volumes of GMELIN'S 'Chemistry' the stock has by this means been greatly reduced, so that only a limited number of some of the volumes remain on hand, and for some time past there has been none of the first volume left. The Council are happy to say that they have made an advantageous arrangement with the printers, and the agent, Mr. HARRISON, for the reprinting of the first volume of the 'Handbook' without entailing any pecuniary responsibility on the Society, and Members or others whose sets of the work are deficient of this volume may now obtain it at 59, Pall Mall. The re-issue of this volume also enables the Council to make up a few complete sets from Vol. 1 to Vol. 12 inclusive, which will be supplied for six guineas, the previously existing arrangement for the disposal of sets from Vol. 2 to Vol. 6 being now cancelled. Separate volumes, however, from Vol. 4 upwards, may be obtained, as there are found to be several such left after making up as many complete sets as the early volumes on hand would admit of."

STATEMENT of RECEIPTS and EXPENDITURE of the CAVENDISH SOCIETY, from the 1st of March, 1860,  
to the 26th of February, 1861.

[illegible]

We have examined the above Statement, and find it correct,

February 26th, 1861.

ALFRED SMEE,  
THOMAS HYDE HILLS.

It was resolved—

“That the Report just read be received, approved, and adopted.”

The Meeting then proceeded to the election of Officers for the ensuing year, and the following Gentlemen were declared to have been duly elected:—

### President.

THOMAS GRAHAM, F.R.S.

### Vice-Presidents.

PROFESSOR BRANDE, F.R.S.

WALTER CRUM, F.R.S.

JOHN DAVY, M.D., F.R.S.

CHARLES G. B. DAUBENY, M.D., F.R.S.

TUE DUKE OF DEVONSHIRE, F.R.S.

MICHAEL FARADAY, D.C.L., F.R.S.

JOHN GRAHAM, F.C.S.

A. W. HOFMANN, Ph. D., LL.D.,  
F.R.S.

HENRY BEAUMONT LEESON, M.D.,  
F.R.S.

W. A. MILLER, M.D., F.R.S.

ROBERT PORRETT, F.R.S.

WILLIAM SHARPEY, M.D., F.R.S.

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N. S. MASKELYNE, F.C.S.

TRENHAM REEKS, Esq.

ALFRED SMEE, F.R.S.

J. DENHAM SMITH, F.C.S.

R. D. THOMSON, M.D., F.R.S.

A. W. WILLIAMSON, Ph.D. F.R.S.

COLONEL PHILIP YORKE, F.R.S.

### Treasurer.

GEORGE DIXON LONGSTAFF, M.D., 9, Upper Thames Street.

### Secretary.

THEOPHILUS REDWOOD, Ph. D., 19, Montague Street, Russell Square.

### Collector.

MR. THOMAS WEST, Burlington House, Piccadilly, W.

Agent for the Distribution of Books, &c.

MR. F. HARRISON, 59, Pall Mall, S.W.

It was resolved—

“That Drs. DE LA RUE, ODLING, and STENHOUSE be appointed Auditors for the ensuing year.”

The following Resolutions were unanimously adopted:—

“That the thanks of the Meeting be given to the PRESIDENT, COUNCIL, and OFFICERS, for their services to the Society.”

“That the thanks of the Meeting be given to the HONORARY LOCAL SECRETARIES for their services to the Society.”

“That the thanks of the Meeting be given to the CHEMICAL SOCIETY for the use of their rooms.”

THEOPH

REDWOOD, SECRETARY



## OBJECTS, &c., OF THE CAVENDISH SOCIETY.

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THE Cavendish Society was instituted for the promotion of Chemistry and its allied sciences, by the diffusion of the literature of these subjects.

The subscription, constituting membership, is one guinea a-year, to be paid in advance; and the subscription becomes due on the 1st of January of each year. A member is entitled to a copy of every book published by the Society for the year for which he has subscribed, but no member can receive the Society's publications until his subscription has been duly paid.

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## WORKS OF THE CAVENDISH SOCIETY.

1848.

- 1.—CHEMICAL REPORTS AND MEMOIRS. Edited by THOMAS GRAHAM, F.R.S. (Out of Print.)
- 2.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Translated by HENRY WATTS, B.A., F.C.S. Vol. I.

1849.

- 3.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. II.
- 4.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. III.
- 5.—THE LIFE AND WORKS OF CAVENDISH. By Dr. GEORGE WILSON.

1850.

- 6.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. IV.
- 7.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. V.

1851.

- 8.—PHYSIOLOGICAL CHEMISTRY. By PROFESSOR LEHMANN. Translated by GEORGE E. DAX, M.D., F.R.S. Vol. I. (Out of Print.)
- 9.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. VI.

1852.

- 10.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. VII. (Organic Chemistry, Vol. I.)
- 11.—PHYSIOLOGICAL CHEMISTRY. By PROFESSOR LEHMANN. Vol. II.
- 12.—ATLAS OF PLATES RELATING TO PHYSIOLOGICAL CHEMISTRY. By Dr. OTTO FUNK. (Supplement to LEHMANN'S PHYSIOLOGICAL CHEMISTRY.)

1853.

- 13.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. VIII. (Organic Chemistry, Vol. II.)
- 14.—ELEMENTS OF CHEMICAL AND PHYSICAL GEOLOGY. By PROFESSOR BISCHOF. Vol. I.

1854.

- 15.—THE LIFE AND SCIENTIFIC RESEARCHES OF DALTON. By Dr. W. C. HENRY, F.R.S.  
~~PHYSIOLOGICAL CHEMISTRY~~ By PROFESSOR LEHMANN.

1855.

- 18.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. IX.  
(Organic Chemistry, Vol. III.)  
19.—ELEMENTS OF CHEMICAL AND PHYSICAL GEOLOGY. By  
PROFESSOR BISCHOF. Vol. II.

1856.

- 20.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. X.  
(Organic Chemistry, Vol. IV.)  
21.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. XII.  
(Organic Chemistry, Vol. VI.)

1857.

- 22.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. XI.  
(Organic Chemistry, Vol. V.)

1858.

- 23.—ELEMENTS OF CHEMICAL AND PHYSICAL GEOLOGY.  
By PROFESSOR BISCHOF. Vol. III.

1859.

- 24.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. XIII.  
(Organic Chemistry, Vol. VII.)

1860.

- 25.—HAND-BOOK OF CHEMISTRY. By LEOPOLD GMELIN. Vol. XIV.  
(Organic Chemistry, Vol. VIII.)

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**CHEMICAL REPORTS AND MEMOIRS.** Edited by PROFESSOR GRAHAM. This work is out of print.

**GMELIN'S HAND-BOOK OF CHEMISTRY.** Translated and Edited by HENRY WATTS, B.A., F.C.S.

A few sets remain from Vol. I to Vol. XII, which are supplied for £6 6s. Separate copies of the Volumes from IV to XII may also be had at 10s. 6d. each.

Vols. XIII and XIV can only be obtained by subscribing for the years for which they were issued.

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\*.\* Applications for the works of the Cavendish Society, are to be made to the Agent, Mr. Harrison, 59, Pall Mall, S.W.; by whom also the Subscriptions of Members are received.

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